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Simultaneous Diffusion and Adsorption of Chloroplatinic Acid in Charcoal Pellet during Preparation Process of Supported Platinum Catalyst

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The impregnation of chloroplatinic acid in the two types of charcoal has been studied in this work. Using a mathematical model the impregnation process has been described enabling the calculation of the active component distribution profile through the support pellet. The diffusion and/or adsorption of chloroplatinic acid in the porous charcoal pellet was investigated with respect to the character of chloroplatinic acid solvent used for the impregnation. It was found that the use of an aqueous solution of chloroplatinic acid for impregnation results in the nonuniform distribution of platinum. Uniform platinum distribution can be achieved, when an acetone solution of chloroplatinic acid is used for the impregnation. Calculated distribution profiles were in qualitative agreement with the experimental ones found by electron microanalysis.

The catalysts with uniform platinum distribution were found to be much more resistant to sintering during heat treatment and reduction of catalysts then catalysts with nonuniform distribution. As a result the former had higher catalytic activity in a nitrobenzene and 1-octene liquid phase hydrogenation.

INTRODUCTION

The recognition of the relationship between the metal distribution and dispersion in the grain of supported catalyst is of great importance in the preparation process of the impregnated supported catalyst. Attention was focused in several recent papers (e.g., *1–7*) on the formulation of the mathematical description of the porous support impregnation by an active component. This problem was solved for both the spherical (*1–5*) and cylindrical (*6, 7*) shapes of the support particle. The method of electron microanalysis enables the comparison of the model idea with the existing experimental distribution profiles (*5, 7*) of the active component through the support particle. Greater success in this research is limited by the lack of the pertinent values of the effective diffusion coefficient of the active component in the porous structure of the support. It is also difficult to distinguish the bulk isotropicity of the support grain.

The present paper is aimed at finding reasons which cause a nonuniform distribution of platinum in a catalyst prepared by impregnation of charcoal pellets by chloroplatinic acid solutions. A relation between the platinum distribution and dispersion was investigated with respect to the thermal calcination and/or reduction of the adsorbed chloroplatinic acid by hydrogen. The achieved platinum dispersity in the prepared catalysts was then confronted with catalyst activity measured on 1-octene and nitrobenzene liquid phase hydrogenation.

The relation between the existing preparation conditions of the catalyst, i.e., both calcination and reduction temperature, treatment time, etc. and its catalytic activity during liquid phase hydrogenation was studied in a recent paper (*8*). Details con-

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cerning the catalyst preparation are given in a previous paper (*9*).

THEORETICAL MODEL OF IMPREGNATION PROCESS

In order to formulate the mathematical description of the support impregnation by an active component the following presumptions have to be made: (a) non-steady state, (b) spherical shape of the support grain, (c) previously wetted support, the pores of which are initially filled with the solvent, (d) limited volume of impregnation solution without concentration gradients, i.e., time-dependent concentration of the active component, (e) simultaneous diffusion in pores and adsorption on the inner support surface of the active component, the concentration of which is both the function of coordinate and time, and (f) rate of adsorbate adsorption is more rapid than its diffusion.

Time dependence of active component concentration in support pores is described by the following partial differential equation:

$$\frac{\partial C}{\partial t} = D\left[\left(\frac{\partial^2 C}{\partial r^2}\right) + \frac{2}{r}\left(\frac{\partial C}{\partial r}\right)\right] - \frac{\partial C_a}{\partial t}. \quad (1)$$

Concentration of C_a adsorbate in the equation can be replaced by the value computed from the pertinent adsorption isotherm. Adsorption isotherms are usually expressed as a Freundlich or a Langmuir type isotherm. In the Freudlich relation which can be expressed as

$$C_a = K \cdot C^n \quad (2)$$

diffusion Eq. (1) can be rearranged into the following form:

$$\frac{\partial C}{\partial t} = \frac{D}{\left(1 + \frac{\rho}{\epsilon} Kn\, C^{n-1}\right)} \left[\left(\frac{\partial^2 C}{\partial r^2}\right) + \frac{2}{r}\left(\frac{\partial C}{\partial r}\right)\right]. \quad (3)$$

Using the Langmuir adsorption isotherm

$$C_a = \frac{K_1 C}{1 + K_2 C} \quad (4)$$

the diffusion equation can be written as follows:

$$\left(\frac{\partial C}{\partial t}\right) = \frac{D}{1 + \frac{\rho}{\epsilon}\left(\frac{K_1}{(1 + K_2 C)^2}\right)} \left[\left(\frac{\partial^2 C}{\partial r^2}\right) + \frac{2}{r}\left(\frac{\partial C}{\partial r}\right)\right]. \quad (5)$$

It is necessary to formulate the following initial and boundary conditions with respect to the problem presumption:

$$t = 0 \quad 0 \leq r < R \quad C(r,0) = 0 \quad (6)$$

$$t = 0 \quad r = R \quad C(R,0) = C_0 \quad (7)$$

$$t > 0 \quad r = 0 \quad \frac{\partial C(0,t)}{\partial r} = 0 \quad (8)$$

$$t > 0 \quad r = R \quad C(R,t) = C_s(t). \quad (9)$$

The time function $C_s(t)$ expresses the concentration change of the active component in limited space of volume V around the impregnated support particle. Supposing this space is without gradient the concentration of the active component in it ensures from mass balance

$$C_s(t) = C_0 - \frac{4\pi}{V}\int_0^R \left(\frac{\rho}{\epsilon} K \cdot C^n + C\right) r^2\, dr. \quad (10)$$

The system of Eqs. (3), (6)–(10), and (5)–(10) was solved using a finite difference method.

Although charcoal pellets impregnated in this study had a cylindrical shape, the theoretical model was formulated for a spherical case in order to simplify its numerical solution. The equivalent radius of the support pellets was then considered as:

$$R = 3V_p/S_p. \quad (11)$$

EXPERIMENTAL

Kinetics and equilibrium of support impregnation. Commercial charcoals Supersorbon H8-3 (Degussa) and Norit RB1

(Norit) were employed for impregnation by aqueous and acetone solutions of chloroplatinic acid (analytical grade, Safina Vestec).

Supersorbon H8-3 and Norit RB1 charcoal pellets had cylindrical shapes (diameters 4 and 1 mm, lengths 6 and 4 mm, respectively).

Prior to any impregnation the support was boiled in a pure solvent in order to fill the support pores with a solvent. The impregnation was carried out in the apparatus described elsewhere (*9*).

The support was poured into a Teflon basket which was placed in a thermostated cylindrical vessel with a solution of chloroplatinic acid. Using a mechanically agitated stirrer which was located in the axis and near the bottom of the vessel, this solution circulated through the fixed bed of the support. The initial concentration of chloroplatinic acid was in accordance to the 5% wt. platinum in the prepared catalyst. In the course of the impregnation process the concentration of chloroplatinic acid in the solution was measured using a SPECOL colorimeter (Zeiss, GDR) at wavelength 400 nm.

The impregnation process was stopped when the concentration of chloroplatinic acid dropped to zero (in impregnation from an aqueous solution) or the system reached equilibrium (in the case of acetone solution). The adsorption isotherms were measured after the system had reached equilibrium. It was found experimentally that the time of impregnation, 15 hr, is sufficiently long to reach this equilibrium. The initial chloroplatinic acid concentration was changed in the range 2–60 g/liter. Both the impregnation process and the equilibrium measurements were carried out at 20°C.

Catalyst preparation. A detailed preparation process of the platinum catalyst was described in recent papers (*9*, *10*). The support impregnated by a chloroplatinic acid solution was dried at 60°C in a vacuum rotary evaporater, and the pellets were then placed into an electrical furnace where the catalyst was calcinated in a fixed bed in a nitrogen atmosphere and then reduced in the hydrogen flow at constant temperature (100, 200, and 300°C). The required time of both calcination and reduction was previously found (*10*) due to the testing of the hydrogen chloride content of gas leaving the reduction furnace. After the reduction the catalyst was passivated in a stream of cold nitrogen and the pellets were crushed and sieved to a required size for a catalyst activity measurement (<0.050 mm) and a H–O titration measurement of platinum dispersity (0.3–0.6 mm).

Catalyst activity measurement. The activity of a catalyst was determined as an initial hydrogenation rate of nitrobenzene and 1-octene, respectively. Measurements were carried out in ethanol in a batch stirred tank reactor at 25°C and atmospheric pressure of hydrogen. Further details concerning the apparatus and procedure were previously (*14*, *15*) described.

Platinum dispersity measurement. The mean size of the platinum crystallites was determined by two different methods: X-ray diffraction (XRLB) and H–O titration. The X-ray broadening of the Pt (111) line was measured using a Geigerflex D-6-C diffractometer with an S 6-7 goniometer (Rigaku Denki, Ltd), anode CuK_α. The mean size of the platinum particles was evaluated by measuring the width diffraction lines at half height and then applying Scherrer's formula (*13*).

The hydrogen–oxygen titration measurements were carried out at ambient temperature in a pulse flow device with the thermoconductivity detection of adsorbate. The used apparatus was similar to that described by Freel (*11*). The measurement procedure was performed according to Prasad *et al.* (*12*). The catalyst amount (1–2 g) was crushed to a grain diameter of 0.3–0.6 mm. The mean platinum crystallite size was evaluated from titration measurements on the base of stoichiometry (*12*) HC : OC : HT = 1 : 0.5 : 2

$$d_{\mathrm{HO}} = 6 \times 10^6 \mathrm{m/Pt} \cdot \mathrm{S}. \qquad (12)$$

Measurement of platinum radial distribution profile in catalyst pellet. Platinum radial distribution profiles in the catalyst pellet were measured using electron microanalysis. The measurements were carried out with a JEOL JSM 50-A scanning electron microscope with an EDAX-711 energy-dispersion X-ray detector. The reduced and pasivated catalyst pellets were cut perpendicular to the cylinder axis in the center of the cylinder. The analysis was carried out along the diameter of this cross-section by means of a line scan procedure. The measured dependence of X-ray intensity corresponding to M_α line Pt on a radial coordinate of catalyst pellet was recalculated on a platinum concentration profile using the known mean analytically given concentration of platinum in a prepared catalyst.

RESULTS AND DISCUSSION

Impregnation Kinetics and Adsorption Equilibrium

The present work is aimed at the impregnation of two charcoal species by chloroplatinic acid dissolved in two very different media—water and/or acetone. The influence of the solvent nature upon time dependence of chloroplatinic acid concentration in impregnation solution for Degussa and Norit supports are shown in Figs. 1 and 2, respectively. It is obvious that the impregnation process is much more rapid in an aqueous solution than in an acetone one. Moreover in the case of a solution of chloroplatinic acid in water the adsorbed amount of chloroplatinic acid is higher. While using an acetone solution the system reaches an equilibrium concentration after a satisfactorily long time interval. The competitive adsorption of both active component and solvent on the support surface changes in a natural way the adsorption capacity of the support for the active component.

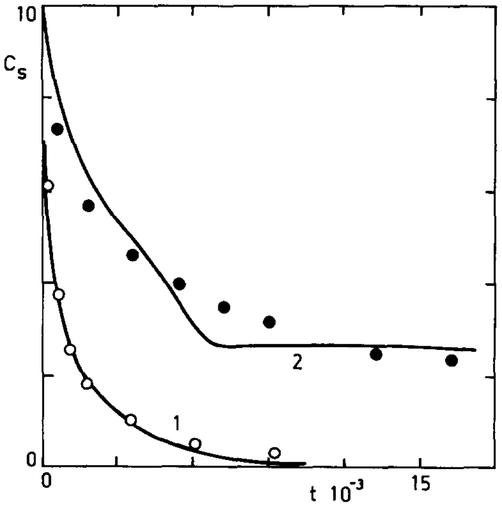

FIG. 1. Experimental and computed time dependences of the chloroplatinic acid concentration in impregnation solution—support Degussa: (1) water; (2) acetone.

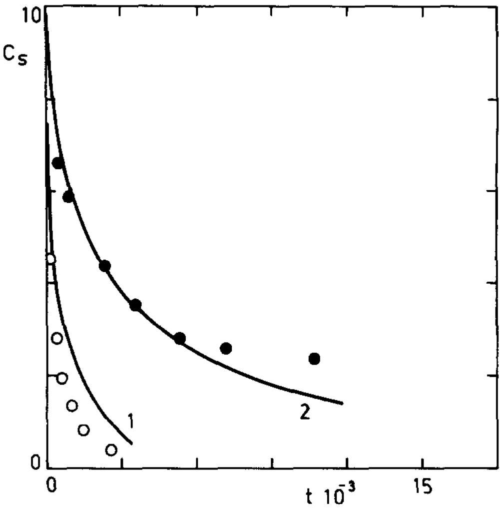

FIG. 2. Experimental and computed time dependences of chloroplatinic acid concentration in impregnation solution—support Norit: (1) water; (2) acetone.

The different properties of both solvents are also evident from the experimental adsorption isotherms, the parameters of which are presented in Table 1. The initial rates of the impregnation process are also given in this table. Using quasilinear regression analysis it was found that experimental adsorption data of Supersorbon H8-3 Degussa impregnation are satisfactory for the Freundlich's isotherm, and the Norit

TABLE 1

Adsorption Isotherms of Chloroplatinic Acid and Initial Rates of Support Impregnation

Activated carbon	Solvent	Isotherm	r^0 (s^{-1})
Degussa H8-3	Water	$C_a = 0.25C^{0.19}$	8.5×10^{-4}
	Acetone	$C_a = 0.07C^{0.33}$	2.1×10^{-4}
Norit RB1	Water	$C_a = 0.4C/(1 + 0.75C)$	1.8×10^{-3}
	Acetone	$C_a = 0.2C/(1 + 0.79C)$	3.4×10^{-4}

RB1 impregnation corresponded with the Langmuir one. Thus the applied mathematical model was solved with respect to both adsorption isotherms. All parameters of the model are summarized in Table 2.

Platinum Distribution Profiles

The computed concentration profiles of the active component in the charcoal Degussa particle (both in pores and in adsorbed state on the support surface) are shown in Figs. 3 and 4. The concentration profiles are presented for different values of the dimensionless parameter $D_{eff}\ t/R^2$ for both solvents used—water (Fig. 3) and acetone (Fig. 4).

It is evident that the distribution of the active component in the catalyst particle depends on the solvent of the chloroplatinic acid. When using an aqueous solution of chloroplatinic acid for an impregnation the active component is located mainly in the external part of the support particle. On the other hand using an acetone solution of chloroplatinic acid for impregnation results in a uniform platinum distribution profile.

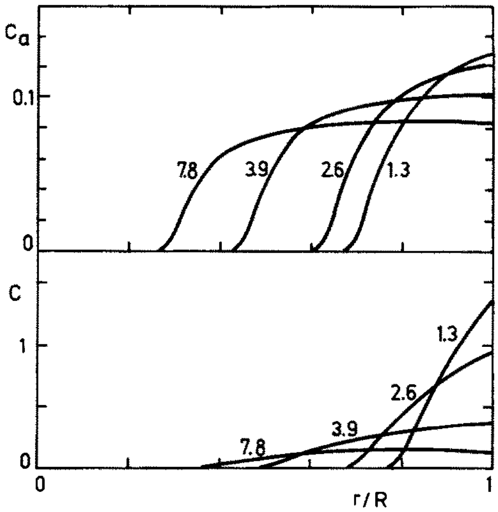

FIG. 3. Computed platinum concentration profiles in catalyst pellet—support Degussa: (lower) platinum profiles in pores; (upper) surface adsorbed platinum profiles (number at curve is dimensionless time, $D_{eff}\ t/R^2$).

A comparison of the computed concentration profile of chloroplatinic acid adsorbed on the inner surface of the support with platinum profiles measured on the cross-section of the catalyst particle, presented for Charcoal Degussa in Fig. 5, is very interesting. The platinum profile was measured after the calcination and reduction of the impregnated support. It could be claimed that Figs. 3 and 4 predict the experimental data of Fig. 5.

Experimental results in Fig. 5 are in qual-

TABLE 2

Effective Diffusion Coefficients of Chloroplatinic Acid in Charcoal (20°C)

Activated carbon	Solvent	Dimensionless time $D_e t/R^2$ (—)	Time (s)	D_{eff}[a] (m^2/s)	D_{eff}[b] (m^2/s)
Degussa H8-3	Water	2.6	7200	1.9×10^{-9}	1.1×10^{-8}
	Acetone	0.31	3600	4.5×10^{-10}	2.7×10^{-9}
Norit RB1	Water	5.5	2400	1.1×10^{-9}	3×10^{-9}
	Acetone	7.8	9000	4.2×10^{-10}	3.8×10^{-10}

[a] D_{eff}, value evaluated from a comparison of the computed and measured platinum distribution profiles.

[b] D'_{eff}, value evaluated from a comparison of the computed and measured impregnation kinetic data.

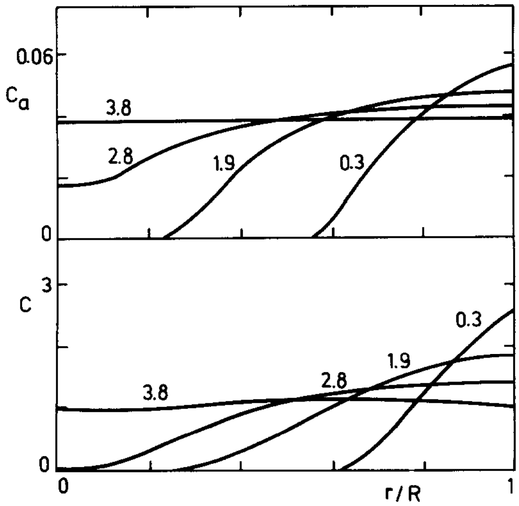

FIG. 4. Computed platinum concentration profiles in catalyst pellet—support Degussa impregnated by acetone solution (see legend to Fig. 3).

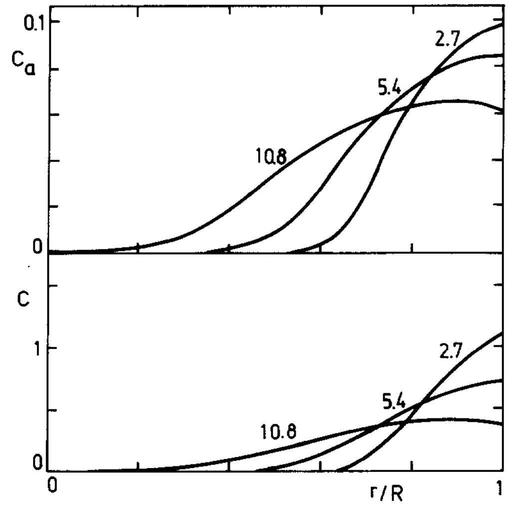

FIG. 6. Computed platinum concentration profiles in catalyst pellet—support Norit impregnated by aqueous solution (see legend to Fig. 3).

itative agreement with the profiles followed from the solution of the mathematical model (see Figs. 3 and 4).

The same situation was found in the case of the Norit RB1 support. Figures 6 and 7 present the computed platinum concentration profiles through the catalyst pellet for aqueous and acetone solutions of chloroplatinic acid, respectively. The experimental results in Fig. 8 prove that the measurements and model solution are in accordance. The prepared catalyst from the acetone solution of the active component had a nearly uniform distribution of platinum on the cross-section of the particle.

A comparison of the measured and calculated platinum profiles through the particle enables us to estimate values of the effec-

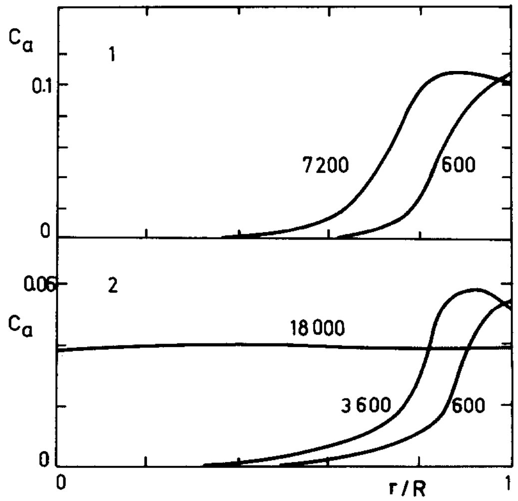

FIG. 5. Experimental platinum distribution profiles in catalyst pellet—support Degussa: (1) water; (2) acetone (number at curve is impregnation period).

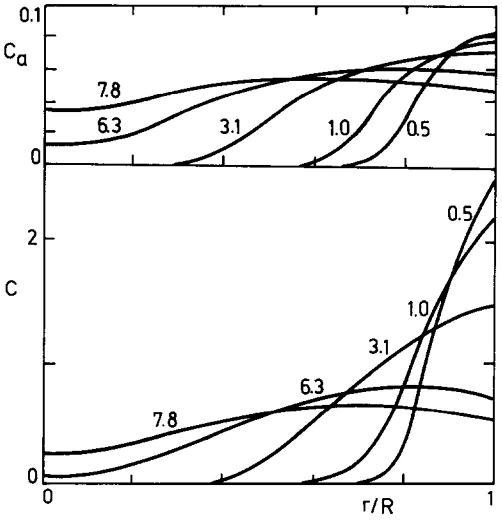

FIG. 7. Computed platinum concentration profiles in catalyst pellet—support Norit impregnated by acetone solution (see legend to Fig. 3).

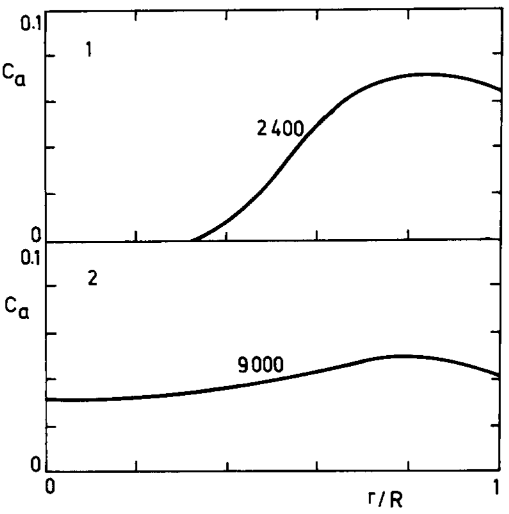

FIG. 8. Experimental platinum distribution profiles in catalyst pellet—support Norit (see legend to Fig. 5).

tive diffusivity of chloroplatinic acid in the porous structure of the support. These values of the diffusion coefficients were compared in Table 2 with coefficients determined from the fitting of the calculated time dependence of chloroplatinic acid concentration in the impregnation solution to the experimental data. As follows from Table 2 the Degussa diffusion coefficients determined in these two ways differ in magnitude by one order. The explanation of observed difference is not simple. The cause of this phenomena may consist in, e.g., the strong adsorption of the active component in the crust of the support which may result in the unisotropicity and/or time-dependent properties of the solid phase in its cross-section. A real explanation however will require intensive further research.

In the case of Norit RB1 very good agreement in the values of the effective diffusion coefficient estimated from both distribution profiles and impregnation kinetic data (see Table 2) was achieved.

From the given results it may be concluded that the two studied species of activated carbon have different adsorption properties.

Platinum Catalyst Properties

Platinum distribution was found to have a considerable influence on platinum dispersity and consequently also on the achieved catalytic activity of the catalyst prepared at various temperatures during calcination

TABLE 3

The Platinum Dispersity and Catalytic Activity of the Catalysts Prepared

Activated carbon	Solvent	Reduction temperature (°C)	Activity (mmol $H_2/g_{Pt} \cdot$ sec)		Mean platinum crystallite size (nm)	
			Octene	Nitrobenzene	d_{XRLB}	d_{HO}
Degussa H8-3	Water	100	3.90	2.41	4	3.7
		200	1.55	1.58	8.1	7.7
		300	0.89	2.16	17.2	30.4
	Acetone	100	5.34	2.91	5.4	4.7
		200	4.08	2.73	9.1	8.4
		300	4.19	2.80	8.4	8.2
Norit RB1	Water	100	5.59	2.38	4	3.6
		200	2.01	1.41	8.4	—
		300	0.77	0.77	13.7	14.3
	Acetone	100	7.43	4.04	4	—
		200	1.95	0.86	8.7	—
		300	1.18	0.74	10.1	—

and reduction. Experimental results of catalytic activity in nitrobenzene and 1-octene hydrogenation are summarized in Table 3. The measured values of platinum dispersity using both H–O titration and X-ray diffraction methods are also given in this table. On the bases of results presented in Table 3 we may conclude that the uniform platinum distribution gives rise to more advantageous catalytic properties. In this case the matter of sintering of platinum crystallites at given conditions of catalyst is not so important. Among others this fact is evident from the dependence of the mean crystallite size of the platinum upon the preparation temperature of the catalyst (see Table 3).

In conclusion it is possible to state that the competitive adsorption of the active component and the solvent used for the porous support impregnation has a decisive influence on the metal distribution achieved in the catalyst grain. The nonuniformity of the active component distribution increases the potentiality of the metal crystallites sintration which lowers the catalyst activity. Simultaneously it is possible to state that the model solution described qualitatively the impregnation process of charcoal by chloroplatinic acid solutions and that the model presumptions are in accordance with reality.

NOMENCLATURE

C	Solute concentration (kg/m^3)
C_a	Concentration of adsorbed solute (kg/kg)
C_0	Initial solute concentration (kg/m^3)
C_s	Concentration of solute in volume V (kg/m^3)
D, D_e, D_{eff}	Effective diffusion coefficient (m^2/s)
d_{HO}	Mean platinum particle size evaluated from H–O titration (nm)
d_{XRLB}	Mean platinum particle size evaluated from XRLB measurements (nm)
K	Constant of Freudlich's isotherm
K_1, K_2	Constants of Langmuir's isotherm
m	Total platinum load in catalyst (—)
n	Constant of Freundlich's isotherm
r	Radial coordinate (m)
r^0	Initial impregnation rate (s^{-1})
R	Radius of the pellet (m)
S	Metal surface area (m^2/kg)
S_p	External surface of the pellet (m^2)
t	Time (s)
V	Volume around one impregnated support particle (m^3)
V_p	Volume of the pellet (m^3)

Greek Symbols

ϵ	Porosity (—)
ρ	Apparent density of the support (kg/m^3)
ρ_{Pt}	Platinum density (kg/m^3)

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