

## DETERMINATION OF STRUCTURE PARAMETERS OF PLATINUM HYDROGENATION CATALYSTS AND THEIR SUPPORTS

Jiří RŮŽIČKA<sup>a</sup>, Jiří HANIKA<sup>a</sup>, Zdeněk SEDLÁČEK<sup>b</sup> and Vlastimil RŮŽIČKA<sup>a</sup>

<sup>a</sup> Department of Organic Technology and

<sup>b</sup> Department of Physical Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6

Received February 10th, 1987

Six catalysts containing 5 and 6.1 wt. % Pt were prepared by impregnation of activated carbon (Atlas AET 300) with  $H_2PtCl_6$  from aqueous solutions and subsequent calcination and reduction with hydrogen at 100, 200, and 300°C. The specific surface area was determined for the catalysts, saturated supports and the untreated support. The adsorption isotherms of n-pentane at 0°C were measured for the support, saturated support and catalyst (100°C), and the experimental data were correlated by the BET, Langmuir, and Dubinin equations; the pore radii distribution was also calculated for them. The activities of the catalysts were evaluated by measuring the initial reaction rates of hydrogenation of 1-octene and nitrobenzene.

Heterogeneous catalysts play a very important role in today's chemical industry. Most of them are porous substances possessing large surface areas. The surface area and surface quality of a catalyst are determined by the support, particularly for catalysts prepared by impregnation. Among reactions for which heterogeneous catalysis is a conventional approach are hydrogenations<sup>1</sup>, where precious metals deposited on suitable supports are frequently used as catalysts<sup>2</sup>. The effect of nature of the support on the properties of the catalyst has not been discussed in detail by Rylander in his monograph<sup>2</sup>, although data exist concerning the effect of support not only on the activity of metallic hydrogenation catalysts<sup>1</sup> but also on their selectivity (e.g., hydrogenation of halogenated aromatic nitro compounds<sup>3</sup>). It has been demonstrated<sup>4,5</sup> that properties of the solid phase such as porosity, pore radii distribution, etc., may be altered significantly during the catalyst preparation. Unfortunately, no evidence has been presented in ref.<sup>4</sup> of a relation between the pore structure of the catalyst and its activity, moreover, the measurements have been performed by the mercury porometry method which gives a picture of the structure of the material somewhat different from that derived from the sorption methods used in this work.

The aim of the present study was to investigate changes in the texture parameters of the material during the catalyst preparation and to relate them to the catalyst activity.

## EXPERIMENTAL

*Chemicals.* Activated carbon Atlas AET 300 (Atlas Chemical Industries, Everberg, Belgium),  $S_{\text{BET}} = 850-1150 \text{ m}^2 \text{ g}^{-1}$ ,  $V_p = 0.75-0.85 \text{ cm}^3 \text{ g}^{-1}$ ,  $V_{\text{MAP}} = 0.30 \text{ cm}^3 \text{ g}^{-1}$ , extrudates  $8 \times 3 \text{ mm}$  were boiled in distilled water for an hour prior to use. Hexachloroplatinic acid (Safina, Vestec) was used in aqueous solution, 250 g hexachloroplatinic acid  $1^{-1}$ . Ethanol, denatured with 10% methanol (Spojené lihovary, Prague), was rectified and its azeotropic mixture with water (b.p.  $78^\circ\text{C}$  at 98.1 kPa) was used; nitrobenzene pure (Lachema, Prague) was distilled prior to use (b.p.  $91^\circ\text{C}$  at 1.33 kPa); 1-octene pure (Fluka, Buchs, Switzerland), 98% by GC; n-pentane (Spolana, Neratovice), spectrally pure; nitrogen for lamps and hydrogen of technical purity, B quality, electrolytic (both Technoplyn, Prague).

*Preparation of catalysts.* The support was impregnated with aqueous solution of  $\text{H}_2\text{PtCl}_6$  in a fixed bed apparatus<sup>6</sup> at  $20^\circ\text{C}$ ; the concentration of  $\text{H}_2\text{PtCl}_6$  corresponded to 5 and 10 wt. % Pt on support. The saturated support was treated conventionally<sup>5,7</sup> at 100, 200, and  $300^\circ\text{C}$ . A portion of the dry unreduced saturated support was set aside for adsorption measurements.

An equilibrium established during the impregnation with  $\text{H}_2\text{PtCl}_6$  at the higher concentration, so that the catalyst prepared contained 6.1 wt. % Pt only.

*Specific surface area measurements.* The specific surface area was determined for all catalysts, saturated supports and the untreated support by the nitrogen sorption method, following the procedure by Nelsen and Eggertsen<sup>8</sup> described in detail in Czechoslovak Standard ČSN 01 5185 (ref.<sup>9</sup>).

*Equilibrium adsorption isotherms of n-pentane.* The isotherms were measured<sup>5</sup> in a gravimetric apparatus<sup>10</sup> at  $0^\circ\text{C}$  for the untreated support, support saturated with  $\text{H}_2\text{PtCl}_6$  in a quantity corresponding to 5 wt. % Pt, and catalyst with 5 wt. % Pt reduced at  $100^\circ\text{C}$ .

TABLE I

Specific surface areas of samples

Sorbent	Preparation temperature $^\circ\text{C}$	Platinum content wt. %	Specific surface area $\text{m}^2 \text{ g}_s^{-1}$
Support (Atlas AET 300)	—	0	1 133
Saturated support	60	5.0	909
	60	6.1	655
Catalyst	100	5.0	749
		6.1	555
Catalyst	200	5.0	1 192
		6.1	1 163
Catalyst	300	5.0	1 039
		6.1	1 168

*Determination of catalyst activity.* The activity of the catalysts was determined as the initial reaction rates of hydrogenation of 1-octene and nitrobenzene in ethanolic solutions, measured in a perfectly stirred isothermal reactor at 25°C and atmospheric pressure<sup>11,12</sup>.

## RESULTS AND DISCUSSION

*Specific surface area.* The values of the specific surface area of the samples are given in Table I. They are seen to decrease in the individual stages of preparation of catalysts obtained at 100°C, apparently due to the covering of the support surface by molecules of hexachloroplatinic acid and probably, closing of the mesopores and micropores; a secondary pore structure may also form inside the macropores. This secondary structure alters additionally on the reduction of the catalyst.

The data obtained agree with the previous observations<sup>4,5</sup> that platinum deposited on activated carbon in low concentrations does not affect substantially its specific surface area.

*Equilibrium adsorption isotherms of n-pentane.* The isotherms are shown in Figs 1a–3a. The data indicate that Atlas AET 300 activated carbon has a typical micro-

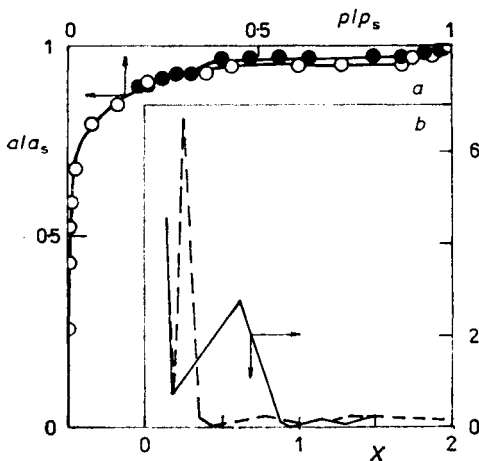


FIG. 1

Atlas AET 300 activated carbon. *a* Equilibrium adsorption isotherm of n-pentane, ● denotes desorption. *b* Differential distribution curve; ——— Brunauer modelless method, - - - cylindrical pore shape concept according to Pierce.  $X = \log \langle r_p \rangle$ ,  $Y = 10^2 (dV_p/d \log \langle r_p \rangle)$

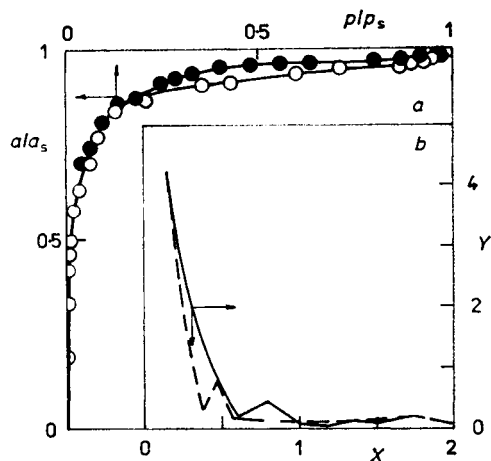


FIG. 2

Atlas AET 300 activated carbon saturated with  $H_2PtCl_6$  (5 wt. % Pt in catalyst). *a* Equilibrium adsorption isotherm of n-pentane, ● denotes desorption. *b* Differential distribution curve; symbols as in Fig. 1

porous structure. The adsorption data were treated in terms of three equations, *viz.* the Langmuir, BET, and Dubinin–Radushkevich<sup>13</sup> adsorption isotherms. Regression analysis gave evidence that the best fit is obtained with the Dubinin–Radushkevich equation,

$$\begin{aligned} n_s &= (W_0/V_M) \exp \left\{ -(k_1/\beta_{\text{aff}}^2) [RT \ln (p_s/p)]^2 \right\} = \\ &= (W_0/V_M) \exp \left\{ -B(T^2/\beta_{\text{aff}}^2) [\log (p_s/p)]^2 \right\}. \end{aligned}$$

Correlation by the linearized form of this equation,

$$\log n_s = \log (W_0/V_M) - 0.434B(T^2/\beta_{\text{aff}}^2) [\log (p_s/p)]^2,$$

is shown in Fig. 4. Although affording overall poorer correlations, the Langmuir equation fits well the adsorption of n-pentane on the saturated support, apparently because of structure changes occurring on the impregnation. The BET equation gives the poorest fit, even in the narrower range of its validity.

For the Dubinin–Radushkevich equation, the values of the constant  $B$  and the mean relative deviations  $e$  between the observed and calculated adsorbed amounts of n-pentane, along with the maximum adsorbed amounts of n-pentane  $a_s$ , are given

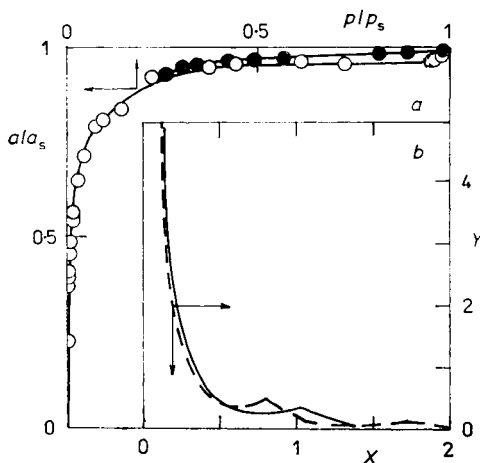


FIG. 3

5 wt. % Pt/Atlas AET 300 catalyst prepared at 100°C. *a* Equilibrium adsorption isotherm of n-pentane, ● denotes desorption. *b* Differential distribution curve; symbols as in Fig. 1

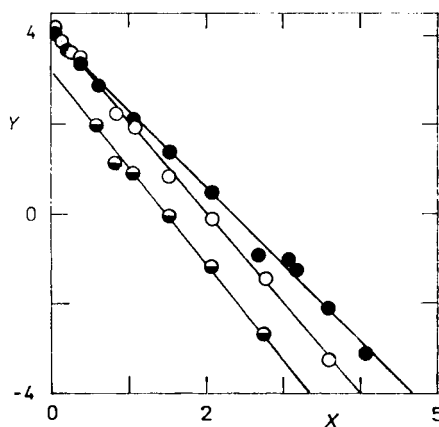


FIG. 4

Correlation of adsorption of n-pentane by the Dubinin–Radushkevich equation. 1 ○ Support saturated with  $H_2PtCl_6$  (5 wt. % Pt in catalyst), 2 ○ 5 wt. % Pt/Atlas AET 300 catalyst, 3 ● Atlas AET 300 activated carbon.  $X = 10^{-5} [\log (p_s/p)]^2$ ,  $Y = 10 \log a$

TABLE II  
Parameters of the Dubinin-Radushkevich equation for the adsorption of n-pentane

Sorbent	$10^{-5}B$	$e$	$a_s$
Support (Atlas AET 300)	0.455	0.88	0.3026
Saturated support	0.554	1.13	0.2472
Catalyst	0.551	0.74	0.2475

TABLE III  
Radii of pores of the highest frequency in samples, calculated by the Brunauer modelless method (ML) and by the Pierce method based on the model of cylidric pore shape (C)

Sorbent	Pore radius, nm	
	ML	C
Support (Atlas AET 300)	1.53	1.62
	1.26	1.31
Saturated support	4.12	2.48
	0.75	0.92
Catalyst	5.48	4.02
	1.04	1.08

TABLE IV  
Activities of catalysts, expressed as the initial reaction rates of hydrogenation of 1-octene  $r_0$  and nitrobenzene  $r'_0$  ( $\text{mmol H}_2 \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ ), in dependence on the treatment temperature and platinum content

Platinum content wt. %	Preparation temperature °C	$r_0$	$r'_0$
5.0	100	6.64	7.19
	300	1.73	3.02
6.1	100	7.16	7.53
	300	1.54	2.31

in Table II. Comparing the  $B$  values (which characterize the sorbent if the same adsorbate is used for all measurements) with those in ref.<sup>5</sup>, the activated carbons Atlas AET 300 and Supersorbon HB-3 are seen to differ significantly.

*Pore radii distribution.* The pore size distribution was calculated for the samples from the desorption data employing Kelvin's equation. The radii of pores of the highest frequency are given in Table III. Figs 1b–3b show the calculated differential distribution curves of the samples. With regard to the limited validity of Kelvin's equation, the plots are only constructed for radii up to 1.2 nm. The data indicate that the porous solid phase undergoes significant structure changes in the transition pore (mesopore) range, during the catalyst preparation; pores with larger radii become most frequent as a result of closing of smaller mesopores and micropores, which is also associated with a reduction of the specific surface area. The measurements and calculations indicate that Atlas AET 300 activated carbon has transition pores with radii about 1 nm, their total volume being small ( $0.04 \text{ cm}^3 \text{ g}_s^{-1}$ ). This implies that this type of activated carbon has basically a bidisperse structure formed by macropores and micropores.

*Catalyst activity.* The activities of four of the catalysts prepared, expressed as the initial reaction rates of hydrogenations of 1-octene and nitrobenzene, are given in Table IV. The initial reaction rate of hydrogenation of nitrobenzene,  $r'_0$ , is higher for the catalysts prepared than for any other catalyst prepared previously by impregnation of activated carbons of other kinds<sup>5,14</sup>; for instance, for the catalyst with 5 wt. % Pt prepared at 100°C it is three times higher than for the catalyst on Supersorbon HB-3 activated carbon prepared in the same conditions<sup>14</sup>, and 1.8 times higher than for the catalyst on Norit 1 Extra activated carbon<sup>15</sup>.

Hydrogenation of 1-octene over this catalyst is also 1.7 times faster than over that with Supersorbon HB-3; only over the catalyst of 5 wt. % Pt on Norit 1 Extra the initial reaction rate of hydrogenation of 1-octene,  $r_0$ , was about 14% higher than over the catalyst treated in this work.

The catalyst of 5 wt. % Pt/Atlas AET 300 thus can be recommended as a highly active catalyst, particularly for the hydrogenation of nitro groups bonded to aromatic rings.

#### SYMBOLS

$a$	adsorbed amount, $\text{g g}_s^{-1}$
$a_s$	maximum adsorbed amount, $\text{g g}_s^{-1}$
$\beta_{\text{aff}}$	affinity parameter of adsorption isotherms
$B$	constant in the Dubinin–Radushkevich equation
$e$	mean relative deviation of calculated and adsorbed amounts, %
$k_1$	constant
$n_s$	adsorbed amount, $\text{mol g}_s^{-1}$

$p$	adsorbate vapour pressure, Pa
$p_s$	adsorbate saturated vapour pressure, Pa
$r_p$	pore radius, nm
$\langle r_p \rangle$	mean pore radius, nm
$S$	specific surface area of sorbent, $\text{m}^2 \text{g}_s^{-1}$
$S_{\text{BET}}$	specific surface area of sorbent by the BET method, $\text{m}^2 \text{g}_s^{-1}$
$V_M$	molar volume of adsorbate, $\text{m}^3 \text{mol}^{-1}$
$V_{\text{MAP}}$	macropore volume of sorbent, $\text{cm}^3 \text{g}_s^{-1}$
$V_P$	pore volume of sorbent, $\text{cm}^3 \text{g}_s^{-1}$
$W_0$	micropore volume of sorbent, $\text{cm}^3 \text{g}_s^{-1}$

## REFERENCES

1. Červený L. (Ed.): *Studies in Surface Science and Catalysis*, Vol. 27. Elsevier, Amsterdam 1986.
2. Rylander P. N.: *Catalytic Hydrogenation over Platinum Metals*. Academic Press, New York 1967.
3. Pajonk G. M., Teichner S. J.: Ref. 1, p. 277.
4. Machek V., Růžička V., Janáček L.: *Collect. Czech. Chem. Commun.* **46**, 1594 (1981).
5. Hanika J., Mansfeld M., Růžička V., Sedláček Z.: *Sb. Vys. Sk. Chem.-Technol. Praze, Org. Chem. Technol. C* **27**, 69 (1981).
6. Machek V., Hanika J., Sporka K., Růžička V.: *Collect. Czech. Chem. Commun.* **46**, 1588 (1981).
7. Uhlíř M., Hanika J., Sporka K., Růžička V.: *Collect. Czech. Chem. Commun.* **42**, 291 (1977).
8. Nelsen F. M., Eggertsen F. T.: *Anal. Chem.* **30**, 1837 (1957).
9. *Czechoslovak Standard ČSN 01 5185*. Published by ÚNM — Úřad pro normalizaci a měření, Prague 1973.
10. Sedláček Z., Růžička V. jr: *Chem. Listy* **67**, 873 (1973).
11. Soukup J., Zapletal V.: *Chem. Listy* **62**, 991 (1968).
12. Hanika J., Sporka K., Růžička V., Deml J.: *Collect. Czech. Chem. Commun.* **42**, 2791 (1971).
13. Dubinin M. M.: *Chem. Rev.* **60**, 235 (1960).
14. Machek V., Růžička V., Šourková M., Kunz J., Janáček L.: *Collect. Czech. Chem. Commun.* **48**, 517 (1983).
15. Machek V.: *Thesis*. Prague Institute of Chemical Technology, Prague 1981.

Translated by P. Adámek.