RELATION BETWEEN THE DISTRIBUTION OF PLATINUM, ITS DISPERSION, AND ACTIVITY OF CATALYSTS PREPARED BY IMPREGNATION OF ACTIVATED CARBON WITH CHLOROPLATINIC ACID SOLUTIONS

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The effect was studied of the solvent of chloroplatinic acid used for impregnation of activated carbon on the distribution and dispersion of platinum and on the catalyst activity. Using different solvents, catalysts were prepared exhibiting either surface platinum distribution (water) or its uniform distribution (ketones). Catalysts with uniform platinum distribution displayed a better stability of the platinum dispersity against sintering. The catalyst activities in liquid phase hydrogenation of 1-octene and of nitrobenzene were related to the platinum dispersity; the results suggest that the hydrogenations of the two substrates are governed by different mechanisms.

Metallic support catalysts are commonly prepared by impregnation of a porous support with solution of a suitable compound of the metal in question[1]. Impregnation of larger support grains always involves the problem of the metal distribution within the particles. The resultant concentration profile is determined by the combined diffusion, adsorption,, and reaction effects involved[2]. Support impregnation can result basically in two cases[1–4]. *1*) The interaction of the solute with the support is strong adsorption by nature; the metal distribution is governed by the sorption-diffusion mechanism and does not change appreciably during subsequent treatment of the catalyst (drying, heat treatment) so-called adsorption catalysts). *2*) The adsorbed quantity of the metal is low as compared with its total concentration (weak adsorption) and the metal distribution changes substantially on subsequent drying or heat treatment of the saturated support (so-called impregnated catalysts).

The catalyst type can be assessed[3] by employing the criterion

$$P = (C_0 - C_r) V / C_r V_p m_n \tag{1}$$

which is the ratio of the amount of the solute that passed from the solution onto the support to that present in the support pores. If $P \gg 1$, the catalyst is adsorption type, if $P \ll 1$, weak adsorption is involved and the catalyst is impregnated type.

In our preceding works[5,6] we have studied the kinetics and equilibrium of adsorption of chloroplatinic acid on activated carbon of various types. Replacement of water by nonaqueous solvents (alcohols, ketones) has been found to appreciably slow down the rate of adsorption and to reduce the maximum quantity of adsorbed chloroplatinic acid. The different solvent effects on the chloroplatinic acid adsorption have been explained in terms of the different ability of the solvents concerned to compete with chloroplatinic acid in the adsorption on activated carbon; this ability has been characterized by the corresponding heats of wetting. Both the adsorption rate and the adsorbed quantity of chloroplatinic acid have been observed to decrease with increasing heat of wetting for the support used. The heats of wetting for organic solvents exceeded essentially the value for water. The competitive sorption of the solvent and chloroplatinic acid necessarily affects also the concentration gradient of the active component within the support grain.

In the present work, the effect has been therefore investigated of the solvent of chloroplatinic acid on the concentration profile of platinum in the catalysts prepared. The effect of the platinum distribution on its dispersity and, thereby, on the catalytic activity has been also examined.

EXPERIMENTAL

Chemicals. Activated carbon Supersorbon H8-3 (Degussa, GFR) extrudates, mean length 6 mm, mean diameter 4 mm. Ethanol denatured with 2% petrol (Spojené lihovary, Prague) rectified prior to use; b.p. 78°C/98·1 kPa. 1-Octene *p.* (Koch-Light, England) distilled prior to use; b.p. 119°C/0·101. MPa. Nitrobenzene *p.* (Lachema-Chemapol, Prague) distilled prior to use; b.p. 91°C/1·33 kPa. 2-Mercaptobenzthiazole *p.a.* (Loba-Chemie, Wien-Fischamend, Austria). Hydrochloric acid *p.a.* (Lachema, Brno). Hydrogen peroxide *p.a.* (Chemical Works. Sokolov). Hydrogen B grade, electrolytical; nitrogen for bulbs; oxygen, unspecified (all Technoplyn, Prague). Helium, min 99·99% (Tega, Leipzig, GDR). Methanol *p.a.*, acetone *p.a.* (both Lachema, Brno). Methyl ethyl ketone *p.a.*, methyl isobutyl ketone pure (both Int. Enc., Ltd., Windsor, England). Hexachloroplatinic acid hexahydrate *p.a.* (Safina, Vestec).

Catalyst preparation. The impregnation of activated carbon, consisting in circulation of the saturating solution through a layer of the support, has been described previously[5,6]. Particles of the impregnated and dried support were placed in an electric furnace and calcinated in nitrogen stream and subsequently reduced in hydrogen stream at a constant temperature (100, 200, or 300°C). The appropriate calcination and reduction periods have been discussed[7,8]. After the reduction, the catalyst was passivated in nitrogen stream at room temperature. The particles then were ground to the size desired for the catalytic activity measurements ($\leqq$0·05 mm) and for the platinum dispersity measurements by hydrogen-oxygen titrations (0·3—0·6 mm).

Determination of the platinum content in the catalyst. Platinum in the catalyst was determined gravimetrically[9] after ignition of the activated carbon and decomposition of the residue with a HCl–H_2O_2 mixture.

Determination of the platinum dispersity. The mean size of the platinum crystallites was measured by two methods: by X-ray diffraction (XRLB) and by hydrogen-oxygen titration (H—O). The broadening of the X-ray lines on the Pt (111) plane was measured on a Geigerflex D-6-C diffractometer with an S6-7 goniometer (Rigaku Denki) using CuK_α radiation. The mean crystallite size was evaluated from the half line width by using Scherrer's equation[10]. The hydrogen-oxygen titration measurements were carried out at room temperature in a flow-through pulse apparatus as described in paper[11], the working procedure was that given in paper[12]. The mean size of platinum crystallites was calculated based on the consumption of hydrogen for titration of chemisorbed oxygen, taking into account the stoichiometry[12] of the chemisorption and hydrogen–oxygen titration HC : OC : HT = 1 : 0·5 : 2, according to the formula

$$d_{\mathrm{HO}} = 6\,.\,10^6 m/\varrho_{\mathrm{Pt}} s\,. \tag{2}$$

Measurement of the radial concentration profile of platinum through the catalyst grain. The platinum distribution was measured by electron microanalysis method on a JEOL JSM 50-A scanning electron microscope combined with an EDAX-711 energy-dispersive X-ray analyzer. A reduced and passivated catalyst particle was cut out perpendicularly to the cylinder axis and analyzed across the section by linear electron microanalysis. The dependence of the X-ray intensity for the Pt M_α line on the radial coordinate of the catalyst grain was converted to the concentration profile of platinum by using the known, analytically determined mean concentration of platinum, assuming that the measured X-ray intensity was proportional to the concentration of the element. The concentration profiles reported in this work represent average values from 4—5 measurements of the X-ray intensity in dependence on the radial coordinate.

The catalyst activity was assessed based on the initial rates of liquid phase hydrogenations of nitrobenzene and 1-octene. The measurements were performed, using ethanol as the solvent, in a discontinuous isothermal stirred reactor at the temperature 25°C and atmospheric pressure of hydrogen. The apparatus and procedure have been described previously[7,13].

RESULTS AND DISCUSSION

Platinum Distribution Profiles

The study was carried out on catalysts prepared by impregnation of activated carbon with solutions of chloroplatinic acid in water, methanol, ethanol, acetone, and methyl ethyl ketone, respectively. Based on our previous results[5,6], Table I gives the initial sorption rates and maximum adsorbed quantities of chloroplatinic acid (determined by extrapolation from the saturated part of the adsorption isotherm). The adsorption kinetics was evaluated to obtain the sorption parameter P. The heats of wetting the activated carbon by the solvents in question are given for illustration too.

As the data in Table I demonstrate, $P \gg 1$ for all of the solvents used, so that the concentration profiles establishing during the saturation can' be regarded invariable during the subsequent treatment. In this connection, an experiment was carried out in which activated carbon was saturated with an aqueous solution of chloroplatinic acid[5,6] and the saturated support was subsequently exposed to contact with ethanol, a solvent with which the lowest value of the sorption parameter was obtained. The concentration profiles of platinum on a support so treated and on activated carbon merely impregnated with aqueous solution of chloroplatinic acid are compared in Fig. 1. The marked similarity of the two distribution profiles again bears out the assumption of the stability of the established concentration profile in the impregnation.

TABLE I

Initial adsorption rate r_a, maximum adsorbed quantity of chloroplatinic acid a_{max}, sorption parameter P, heat of wetting the support Q, and dielectric constant of the solvent ε

Solvent	r_a	a_{max}	P	Q	ε (ref.[16])
Water	250	0·62	1 000	51	80·4
Acetone	28	0·35	48	131	20·7
Methanol	13	0·34	85	135	33·6
Methyl ethyl ketone	8·8	0·31	24	142	18·5
Methyl isobutyl ketone	4·6	—	35	143	—
Ethanol	3·8	0·27	16	146	24·3

TABLE II

Properties of Pt/activated carbon Degussa catalysts prepared from different solutions of chloroplatinic acid

Solvent	C_{Pt} %	Reduction temperature °C	Platinum crystallite size		Catalyst activity	
			d_{XRLB}	d_{HO}	r^0_{ON}	r^0_{NB}
Water	5·0	100	4	3·7	3·90	2·41
		200	8·1	7·7	1·55	1·58
		300	17·2	30·4	0·89	2·16
Methanol	4·3	100	4	5·4	4·60	3·05
		200	9·1	10·2	2·10	2·13
		300	20·0	23·2	0·33	1·00
Ethanol	2·7	100	6·0	5·6	5·81	3·80
		200	7·4	6·8	2·40	2·31
		300	10·0	8·1	2·04	2·56
Acetone	3·9	100	5·4	4·7	5·34	2·91
		200	9·1	8·4	4·08	2·73
		300	8·4	8·2	4·19	2·80
Methyl ethyl ketone	3·2	100	6·0	6·0	5·08	2·58
		200	8·1	8·7	1·86	1·65
		300	10·6	7·5	2·08	1·67
Methyl isobutyl ketone	3·6	100	4	2·5	3·90	2·19
		200	9·7	5·9	2·03	1·41
		300	6·4	3·0	3·23	2·13

The concentration profiles of platinum through the catalyst grain for the various solvents of chloroplatinic acid are shown in Fig. 2. In the solvents tested there clearly appears a transition from pure surface distribution (water) to a uniform distribution of platinum within the catalyst grain (ketones). The solvent effect on the platinum distribution profile, explained in terms of the competitive sorption, is noticeable particularly in the case of saturation with chloroplatinic acid in water and in ketones, respectively. With methanol, a partly non-uniform concentration profile establishes in spite of the competitive sorption.

Generally, apart from the sorption-diffusion mechanism, the concentration profile is determined also by the chemical nature of the support, the solute, and the solvent[14]. In paper[15], for instance, the platinum distribution established on impregnating activated carbon with aqueous and nonaqueous solutions of chloroplatinic acid has been discussed in terms of the different adsorption ability of the dissociated and nondissociated forms of chloroplatinic acid (according to the polarity of the solvent used, Table II).

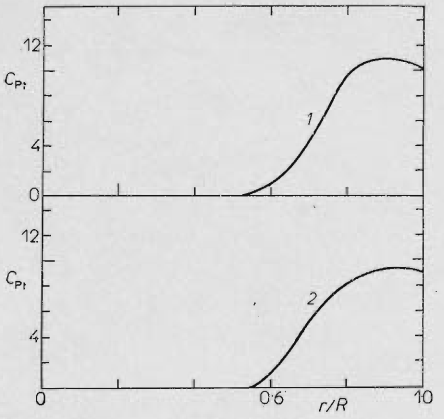

FIG. 1

Platinum concentration profiles through catalyst grain. *1* Impregnation of the support with aqueous solution of chloroplatinic acid. *2* Treatment with ethanol of support impregnated with aqueous solution of chloroplatinic acid

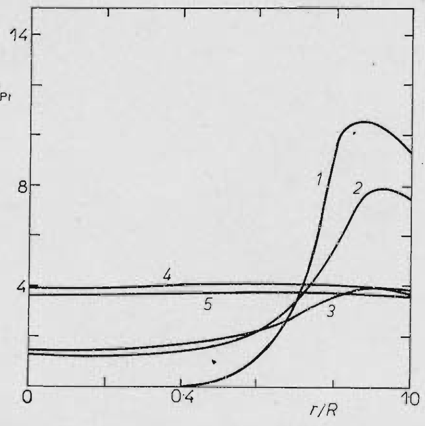

FIG. 2

Platinum concentration profiles through grains of catalysts prepared by impregnating activated carbon with different solutions of chloroplatinic acid; $r/R = 0$: grain centre, $r/R = 1$: grain surface. Impregnation from *1* water, *2* methanol, *3* ethanol, *4* acetone, *5* methyl ethyl ketone

Platinum Dispersity

Based on the known concentration profile of platinum through the catalyst grain it is possible to explain the changes in the metal dispersity occurring on heat treatment of catalysts prepared by using various solutions of chloroplatinic acid. The platinum dispersity expressed as the mean size of the platinum crystallites is given in Table II for the various samples. As the dependence of the mean size of the metal crystallites on the reduction temperature indicates, a uniform distribution of platinum (ethanol, ketone) is favourable for the stability of its dispersity; the crystallites are thus less liable to sintering during the reduction or during application of the catalyst at higher temperatures. The reverse is true in the case of non-uniform platinum distribution (water, methanol), obviously because the metal is concentrated on a considerably smaller area of the support (and, hence, is present in a higher surface concentration) than in the case of a uniform distribution, and consequently, aggregation and formation of larger crystallites is more likely to take place.

Catalyst Activity

The catalyst activity is closely related with the dispersity of the metal on the support surface. The results of the catalytic activity measurements for hydrogenations of 1-octene and nitrobenzene are summarized in Table II. The effect of solvent of chloroplatinic acid on the dispersity, and thereby on the catalyst activity, is apparent from the above discussion; by affecting the platinum distribution profile through the catalyst grain, the solvent influences the dispersity of the metal.

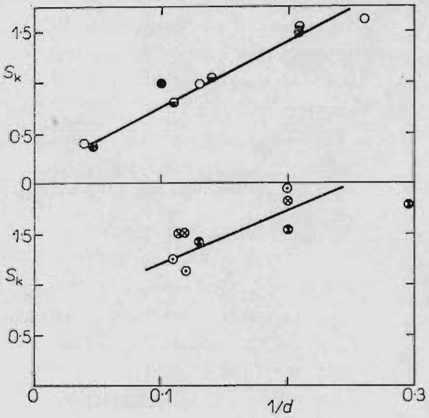

FIG. 3

Correlation between the catalyst selectivity and the platinum dispersity (average value from H—O titration and XRLB measurements). Impregnations from ○ water, ● methanol, ◒ ethanol, ⊗ acetone, ⊙ methyl ethyl ketone, ○ methyl isobutyl ketone

As the data of Table II indicate, the catalysts reduced at a low temperature (100°C) exhibit the highest activity, irrespective of the solvent used; the dispersity is here highest too. As follows from the data for catalysts prepared from a given solvent and reduced at different temperatures, the dispersity of platinum can serve as a measure of the catalyst activity. Interesting considerations can be drawn when the ratio of the reaction rates for hydrogenations of 1-octene and nitrobenzene, in a way characterizing the selectivity of the catalyst, is related to the dispersity or platinum. The dependence of the catalyst selectivity on the platinum dispersity (the mean value from the XRLB and H—O titration measurements) is shown in Fig. 3. For all of the solvents of chloroplatinic acid the ratio of the hydrogenation rates of 1-octene and nitrobenzene increases with the dispersity of platinum, owing to the fact that the catalyst activity in hydrogenation of 1-octene is considerably more sensitive to changes in the platinum dispersity than in hydrogenation of nitrobenzene. Based on the concept of the catalytic activity associated with the dispersity of platinum, it can be thus suggested that the reaction mechanisms involved in hydrogenation of 1-octene and of nitrobenzene are different. From the point of view of the structure sensitivity of chemical reactions[16], the observed results of catalytic activity measurements can be interpreted so that hydrogenations of 1-octene and of nitrobenzene proceed on different kinds of active centres, whose relative occurrence on the metal surface varies with the platinum crystallite size. The above hydrogenations thus may represent model reactions for study of structure sensitivity of chemical reactions.

LIST OF SYMBOLS

a_{max}	maximum adsorbed quantity of H_2PtCl_6 (g/g)
C_O	initial concentration of H_2PtCl_6 in the impregnating solution (g/dm^3)
C_{Pt}	concentration of platinum in the catalyst (%)
C_r	equilibrium (final) concentration of H_2PtCl_6 in the impregnating solution (g/dm^3)
d_{HO}	mean size of platinum crystallite obtained from H—O titration (nm)
d_{XRLB}	mean size of platinum crystallite obtained from XRLB measurement (nm)
m	amount of platinum in the catalyst (g/g)
m_n	support weight for impregnation (g)
P	sorption parameter (Eq. (*1*))
Q	heat of wetting activated carbon (J/g)
r	radial coordinate of catalyst grain (mm)
r_a	initial rate of adsorption of H_2PtCl_6 (mg/g s)
r^0_{NB}	initial reaction rate of hydrogenation of nitrobenzene (mmol H_2/g_{Pt} s)
r^0_{ON}	initial reaction rate of hydrogenation of 1-octene (mmol H_2/g_{Pt} s)
R	radius of catalyst grain (mm)
S	specific surface area of the metal in the catalyst (m^2/g)
S_k	r^0_{ON}/r^0_{NB}, the selectivity of the catalyst
V	volume of the impregnated solution (dm^3)
V_p	pore volume of the activated carbon (cm^3/g)

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