PREPARATION OF Pt/ACTIVATED CARBON AND Pt/ALUMINA CATALYSTS BY IMPREGNATION WITH PLATINUM COMPLEXES

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Activated carbon and alumina catalysts were prepared by impregnation with solutions of platinum compounds differing substantially in the nature of their interaction with the supports: chloroplatinic acid (dissolved in water or acetone), tetraammineplatinum dichloride, and tetrakis (triphenylphosphine)platinum complex. The relations between the course of impregnation, distribution of platinum across the catalyst grain, and the activity of the catalyst in liquid phase hydrogenations were studied. Lower adsorption rates and amounts of the platinum compound adsorbed on the support bring about a more uniform platinum distribution across the grain. Catalysts with a uniform distribution exhibit higher activities than those with nonuniform distribution. The highest activity was achieved with Pt/alumina catalysts prepared from triphenylphosphine platinum complex thermally treated in oxygen atmosphere prior to the reduction.

The first stage of preparation of supported catalysts, *viz.* impregnation of the support with a solution of a compound of the metal of interest, plays an important part in the formation of the catalyst properties. Catalysts with desired properties (distribution and dispersity of the metal, catalyst activity) can be obtained by choosing a suitable system support-compound of the active component-impregnating medium. Among the most significant parameters of the preparation procedures for supported catalysts are the starting compound of the metal and the type of the support.

For platinum support catalysts, chloroplatinic acid is most frequently used as the active component[1,2]; organic complexes of platinum have also been employed[3-5]. Whereas the interaction of inorganic platinum compounds with the support is by nature a more or less strong adsorption, some organic complexes of platinum react with a functional group of the support to form chemical bonds, whereupon a virtually molecular distribution of the active component establishes over the surface, and a highly disperse catalyst can be obtained after the reduction.

This way of preparation has been applied particularly to oxide supports (Al_2O_3, SiO_2), involving surface hydroxy groups[3-5]. Regarding the occurrence of various oxygen-containing groups formed on the surface of activated carbons during the activation, a similar mechanism of surface reaction is conceivable for this type of support as well[6].

The aim of the present work was to examine to which extent the properties of Pt/C and Pt/Al_2O_3 hydrogenation catalysts can be influenced by the choice of the starting platinum compound and the support. The compounds used for the study were hexachloroplatinic (IV) acid, tetraammineplatinum dichloride $[Pt(NH_3)_4]Cl_2$ (a cationic complex), and tetrakis (triphenylphosphine) platinum, $Pt[P(C_6H_5)_3]_4$ (an organocomplex compound), hence platinum compounds whose properties, with respect to the impregnation, are substantially different.

EXPERIMENTAL

Chemicals. Activated carbon (Supersorbon HS-3, Degussa, FRG), cylindric particles 6 mm long, mean diameter 4 mm. γ-Alumina (Condea, Pural S, FRG), cylindric particles 8·5 mm long, mean diameter 1·8 mm. Ethanol (denatured with 2% petrol, Spojené lihovary, Prague) was rectified prior to use; b.t. 78°C/98·1 kPa. 1-Octene *p.* (Koch-Licht, Colnbrook, England) was distilled prior to use; b.t. 119°C/98·1 kPa. Nitrobenzene *p.* (Lachema-Chemapol, Prague) was distilled prior to use; b.t. 91°C/1·33 kPa. Hexachloroplatinic acid *p.a.* (Safina, Vestec). Potassium carbonate *p.*, potassium hydroxide *p.a.*, aqueous ammonia *p.a.*, triphenylphosphine *p.*, potassium bromate *p.a.*, hydrochloric acid *p.a.*, sulphuric acid *p.*, methanol *p.a.*, benzene *p.a.*, acetone *p.a.* (all Lachema, Brno), potassium oxalate *p.a.* (Merck, Darmstadt, FRG), hydrogen peroxide *p.a.* (Chemické závody, Sokolov), 2-mercaptobenzthiazole *p.a.* (Loba-Chemie, Austria).

Synthesis of platinum compounds. Of the platinum compounds used for the preparation of the catalysts, *viz.* chloroplatinic acid, tetraammineplatinum dichloride, and tetrakis (triphenylphosphine)platinum, only chloroplatinic acid is being produced on a commercial scale in Czechoslovakia; therefore, this compound served as the starting substance for the synthesis of the two other substances. An intermediate in their preparation is dipotassium tetrachloroplatinate (II), K_2PtCl_4, obtained by neutralization of chloroplatinic(IV) acid with potassium carbonate followed by reduction with potassium oxalate[7]. Tetraammineplatinum dichloride then was prepared by reacting K_2PtCl_4 with ammonia[8]. Triphenylphosphine platinum complex was obtained by reacting triphenylphosphine with K_2PtCl_4 in an alcoholic solution of KOH (ref.[5]); the complex was dried in vacuum and stored under nitrogen. The two complexes were identified by means of the infrared spectra.

Preparation of the catalysts. The supports were evacuated at 100°C for 4 h, boiled for 1 h in the corresponding solvent, and impregnated in a stationary bed[9] with a circulating aqueous or acetone solution of H_2PtCl_6, aqueous solution of $[Pt(NH_3)_4]Cl_2$, or benzene solution of $Pt[P.(C_6H_5)_3]_4$; the initial platinum concentration in the saturating solutions was invariably 3·8 g/l. The long-term impregnation of the supports with the phosphine complex of platinum was conducted in nitrogen atmosphere. In order to free the material from the weakly sorbed forms of the platinum compounds, the impregnated supports were purged with the pure solvent. Particles of the impregnated and dried support were calcinated in a nitrogen stream and then reduced with hydrogen at 100, 200, or 300°C. After the reduction, the catalyst was passivated in a nitrogen stream at ambient temperature[10]. The catalysts prepared from the phosphine complex were thermally treated in oxygen atmosphere prior to the reduction to ensure a perfect decomposition of the complex[5].

Evaluation of the catalyst properties. The total concentration of platinum in the catalyst was determined gravimetrically after dissolving the sample in a HCl + H_2O_2 mixture. In the case of the Pt/C catalysts the support was ashed before the decomposition[11]. The radial platinum distribution profiles across the catalyst grain and the P/Pt concentrations were measured by employing the electron microanalysis technique[2]. The activity of the catalysts was appraised based on the initial rates of liquid phase hydrogenations of nitrobenzene and 1-octene, measured in a batch isothermal perfectly stirred reactor at 25 °C and atmospheric pressure.

Determination of the concentration of the platinum compound in the impregnating solution. The concentration of chloroplatinic acid in the impregnating solution was measured colorimetrically[9]. Platinum in the tetraammineplatinum dichlorde solution was determined titrimetrically by a method based on the oxidation of the bivalent platinum by potassium bromate in acid solution using methyl orange as indicator[12]. In the tetrakis(triphenylphosphine) platinum solutions, platinum was not determined.

RESULTS AND DISCUSSION

During the contact of a grain of the porous support with the saturating solution, the compound of the active component diffuses into the pores. According to its nature, the metal compound either is more or less strongly sorbed on the support, or reacts chemically with some functional group on the grain surface. In case that the reaction is adsorption, the distribution of the metal within the grain depends on the extent to which the competitive sorption and diffusion of the solvent take place; moreover, the metal compound is bonded in a nonspecific manner giving rise to agglomerates with different numbers of molecules, from which crystallites of the metal are formed on the heat treatment and reduction. Thus the dispersity of the metal within the catalyst and, thereby, the catalyst activity depend above all upon the metal distribution profile across the catalyst grain.

If the interaction of the active component with the support has the character of a chemical reaction, a monomolecular distribution of the metal compound establishes over the support surface; the compound then is decomposed on the heat treatment and reduction, so that ideally a dispersity of unity is attained, *i.e.*, each of the metal atoms is a surface atom.

In this work the starting platinum substances were therefore chosen so that, according to published data, adsorption (H_2PtCl_6) as well as surface chemical reactions ($[Pt(NH_3)_4]Cl_2$, $Pt[P(_6H_5)_3]_4$) was involved. The phosphine complex was chosen with regard to the fact that, unlike other organocomplexes of platinum used for such purposes, it is sufficiently steady over the time typically required for the impregnation.

Impregnation of the supports. The course of impregnation of the supports (Fig. 1) was evaluated in terms of the dependence of the platinum concentration in the saturating solution on the square root of the saturation period, per unit size of the support grain (the supports used differed in the grain size). The maximum amount of platinum sorbed on the support was determined from the segments of the adsorption isotherms corresponding to the saturated state (Fig. 2). For the sake of completeness, the results for the impregnation of activated carbon with chloroplatinic acid, although published previously[2], are included in this paper too. Since for the solutions of triphenylphosphine platinum complex, reproducible results could not be obtained by the available analytical methods (gravimetric analysis, atomic absorption spectrometry), only the experimentally established concentrations of platinum in the catalyst are given in Table I.

The triphenylphosphine complex and, particularly, tetraammineplatinum dichloride are seen to bond onto the two supports to a considerably lower extent than chloroplatinic acid. For a comparison of the platinum concentration calculated from the course of the impregnation (c_i) with the analytically determined concentration inside the catalyst (c_{Pt}) it can be inferred that a great part of tetraammineplatinum dichloride is bonded to the support in so weak a way that it is desorbed on washing the support with the pure solvent. Chloroplatinic acid, on the other hand, is bonded very strongly and cannot be desorbed to an appreciable extent. As follows from the literature[13], platinum complexes with a square planar arrangement (such as the $[Pt(NH_3)_4]^{2+}$ cation) display a lower adsorbing ability than those with an octahedral structure

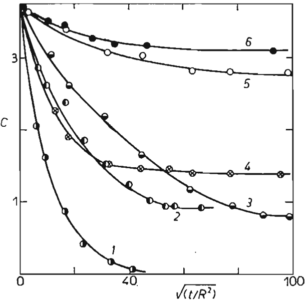

FIG. 1

Time course of impregnation of activated and γ-alumina with platinum compounds. *1* Activated carbon–H_2PtCl_6 (water); *2* activated carbon–H_2PtCl_6 (acetone); *3* alumina–H_2PtCl_6(acetone); *4* alumina–H_2PtCl_6 (water); *5* alumina–$[Pt(NH_3)_4]Cl_2$; *6* activated carbon–$[Pt(NH_3)_4]Cl_2$

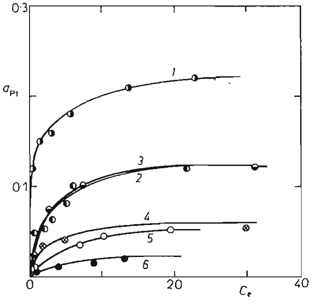

FIG. 2

Adsorption isotherms of platinum compounds on activated carbon and on alumina. *1* Activated carbon–H_2PtCl_6 (water); *2* activated carbon–H_2PtCl_6 (acetone); *3* alumina–H_2PtCl_6 (acetone); *4* alumina–H_2PtCl_6 (water); *5* alumina–$[Pt(NH_3)_4]Cl_2$; *6* activated carbon–$[Pt(NH_3)_4]Cl_2$

the $[PtCl_6]^{2-}$ anion). In the case of carbon supports[14], moreover, their active centres are eported to have electron accepting properties, which also accounts for the considerably lower adsorption of the $[Pt(NH_3)_4]^{2+}$ cation as compared with the $[PtCl_6]^{2-}$anion.

It has been found previously[2,9] that if nonaqueos solvents (alcohols, ketones) are used for chloroplatinic acid in the impregnation of activated carbon the amount of chloroplatinic acid sorbed on the supports drops appreciably (Figs 1, 2); this fact has been explained in terms of the higher ability of organic solvents to compete with chloroplatinic acid in the adsorption on activated carbon.

The present results indicate that in the impregnation of alumina the effect of the solvent of chloroplatinic acid is opposite to that encounterd in the case of activated carbon, water as the solvent suppressing considerably, in comparison with acetone, the adsorption of chloroplatinic acid on alumina (Figs 1, 2). Similarly as in the above case, this fact can be discussed in terms of the competitive sorption of the components in the system H_2PtCl_6–solvent–support. Water sorbs on the hydrophilic alumina to a higher degree than on the hydrophobic carbon, thus competing with the acid in the

TABLE I

Impregnation time t, concentration of platinum in the catalyst calculated after the impregnation c_i and experimentally determined in the ready catalyst c_{Pt}, and maximum adsorbed amount of platinum per unit weight of support a_{max}

Compound	Impregnation time t h	Concentration of Pt c_i %	c_{Pt} %	a_{max} g/g
	Activated carbon			
H_2PtCl_6 (water)	3	5·00	4·98	0·22
H_2PtCl_6 (acetone)	6	3·90	3·72	0·12
$[Pt(NH_3)_4]Cl_2$	6	0·62	0·38	0·022
$Pt[P(C_6H_5)_3]_4$	6	—	0·95	—
	80	—	1·07	—
	Alumina			
H_2PtCl_6 (water)	3	3·20	3·18	0·06
H_2PtCl_6 (acetone)	6	4·31	4·22	0·13
$[Pt(NH_3)_4]Cl_2$	6	1·10	0·19	0·053
$Pt[P(C_6H_5)_3]_4$	6	—	1·08	—
	80	—	1·70	—

sorption; and the reverse is true of the low-polar acetone. Consequences of the competitive sorption of the solvent and the solute are to besought also in the establishment of the concentration gradient of the active component inside the support grain.

Distribution of platinum across the catalyst grain. Generally, any intervention into the impregnating system that accelerates the diffusion or lowers the adsorption of the compound of the active component on the support results in a more uniform distribution of the metal. The concentration profiles of platinum across the grains of the Pt/activated carbon and Pt/alumina catalysts are shown in Figs 3 and 4. The uniformity of the platinum distribution within the grain was found to increase with decreasing sorbed amount of the platinum compound, hence in the order H_2PtCl_6 (water) $<$ H_2PtCl_6 (acetone) $\approx$ $Pt[P(C_6H_5)_3]_4$ $\approx$ $[Pt(NH_3)_4]Cl_2$ for activated carbon, and H_2PtCl_6 (acetone) $<$ H_2PtCl_6 (water) $\approx$ $Pt[P(C_6H_5)_3]_4$ $\approx$ $[Pt(NH_3)_4]Cl_2$ for alumina.

Pt/Al_2O_3 catalysts prepared from tetraammineplatinum dichloride contained platinum in a very low concentration (0·2%), which was at the limit of resolution by the electron microanalysis method, so that the platinum concentration profile could not be plotted reliably enough; on the other hand, this gives evidence that the metal

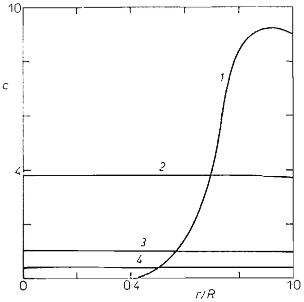

FIG. 3

Concentration profiles of platinum through grains of Pt/activated carbon catalyst. $r/R = 0$: grain centre, $r/R = 1$: grain edge; *1* H_2PtCl_6 (water); *2* H_2PtCl_6 (acetone); *3* $Pt[P(C_6H_5)_3]_4$; *4* $[Pt(NH_3)_4]Cl_2$

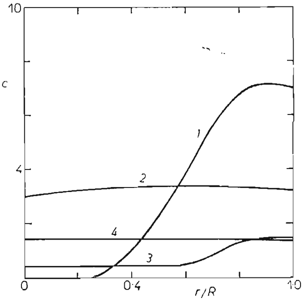

FIG. 4

Concentration profiles of platinum through grains of Pt/alumina catalyst. $r/R = 0$: grain centre, $r/R = 1$: grain edge; *1* H_2PtCl_6 (acetone) *2* H_2PtCl_6 (water); *3* $Pt[P(C_6H_5)_3]_4$, 6 h impregnation; *4* $Pt[P(C_6H_5)_3]_4$, 80 h impregnation was not adsorbed on a local part of the grain cross section, but was evenly distributed across the grain.

When alumina was impregnated with chloroplatinic acid in aqueous solution, a uniform distribution of platinum within the grain was obtained, whereas with acetone as solvent the distribution was non uniform. This fact, again, is contrary to the case of activated carbon, thus supporting the concept of the different competitive sorption of water and acetone in the impregnation of alumina and of activated carbon with chloroplatinic acid, as discussed above.

Activity of the catalysts. There are two ways in which the properties of the platinum compound used for the impregnation affect the catalyst activity. According to the extent to which the compound is adsorbed (as characterized, *e.g.*, by the adsorbed amount), catalysts with surface or uniform distribution of the metal through the grain can be prepared. The shape of the distribution profile then plays an important part in the attaining of a certain level of dispersity and, consequently, catalyst activity[2]. If during the impregnation the platinum compound bonds to some functional

TABLE II

Activity of the catalysts, per unit amount of platinum, in hydrogenations of 1-octene and nitrobenzene

Platinum compound	Reduction temperature °C	Catalyst activity, mmol·H_2/g_{Pt} s, in the hydrogenation			
		octene		nitrobenzene	
		Pt/C	Pt/Al_2O_3	Pt/C	Pt/Al_2O_3
H_2PtCl_6 (water)	100	3·9	6·9	2·4	5·5
	200	1·6	7·1	1·6	8·2
	300	0·9	7·9	2·2	6·9
H_2PtCl_6 (acetone)	100	5·4	4·4	2·9	5·4
	200	4·1	5·2	2·7	6·2
	300	4·2	5·8	2·8	5·4
$[Pt(NH_3)_4]Cl_2$	100	4·1	4·4	2·4	5·6
	200	3·1	5·0	3·3	8·5
	300	2·7	8·3	2·7	9·3
$Pt[P(C_6H_5)_3]_4$	200[a]	—	1·4	—	2·9
	300[a]	0	3·4	0	4·9
	300[b]	2·4	3·5	2·4	4·2

Impregnation period: [a] 6 h; [b] 80 h.

groups of the support by interaction of chemical nature, molecular distribution of the compound over the support surface takes place and a catalyst with a high activity emerges.

The supports impregnated by the platinum compounds in question were reduced at temperatures of 100, 200, or 300°C. The catalyst activities found in hydrogenations of octene and nitrobenzene are given in Table II. Catalysts, of both types, with

TABLE III

Catalyst activity in hydrogenations of octene and nitrobenzene for catalysts prepared from triphenylphospine platinum complex, per unit amount of platinum

Support	Time of oxygen treatment h	Temperature of oxygen treatment °C	Catalyst activity, mmol H_2/g_{Pt} s	
			octene	nitrobenzene
Activated carbon	0[a]	—	0	0
	9[a]	200	2·4	1·9
	0[b]	—	2·4	2·0
	9[b]	200	2·7	2·2
Alumina	0[a]	—	3·4	4·9
	9[a]	300	6·9	7·5
	0[b,c]	—	3·5	4·2
	9[b,d]	300	10·2	11·7

[a] Impregnation period 6 h; [b] impregnation period 80 h; [c] P/Pt = 0·5 (content of P measured by electron analysis); [d] P/Pt = 0·6 (content of P measured by electron microanalysis).

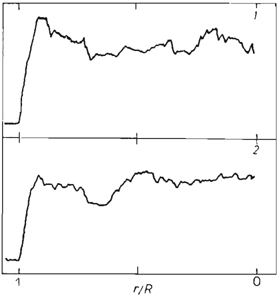

FIG. 5

Profiles of platinum and phosphorus signals, obtained by electron microanalysis, in Pt/ /activated carbon catalyst prepared from the triphenylphosphine complex and only reduced at 300°C. $r/R = 0$: grain centre. $r/R = 1$: grain edge; *1* Pt; *2* P a uniform distribution of platinum exhibit a higher activity. The Pt/alumina catalysts were invariably found more active than the Pt/activated carbon catalysts. As follows from Table II, catalysts prepared by using triphenylphosphine platinum complex in the given conditions (applied in the preparation of catalysts from chloroplatinic acid[2,10]) show the lowest activity; a Pt/C catalyst obtained by a short-term impregnation with the complex was even virtually inactive. The straightforward explanation of this fact is that the used conditions of reduction are not severe enough to bring about a complete decomposition of the phosphine complex. To verify this assumption, the concentration profiles within the grain were recorded for both platinum and phosphorus. A qualitative dependence of the X-ray intensities corresponding to the M_α(Pt) and K_α(P) lines on the radial coordinate of the catalyst grain, as viewed on the working CRT of the electron microscope, was shown in Fig. 5. An overlap of the two profiles is seen; hence, phosphorus occurs at platinum-containing sites.

Triphenylphosphine complexes are reported[5,15] to be highly stable in hydrogen, and only a long-term treatment under oxygen at temperatures above 200°C leads to their decomposition. In our previous work[16], catalysts prepared from the phosphine complex were subjected to heat treatment in oxygen atmosphere before the reduction. For the sake of completencess, selected conditions for the preparation of these catalysts and their properties are given in this paper in Table III. All of the catalysts listed were reduced in identical conditions at 300 °C.

The maximum applicable temperature of the oxygen treatment of Pt/activated carbon catalysts was found to be 200°C; above this temperature the support is ignited. For Pt/alumina catalysts, a significant improvement of the catalyst activity could be achieved by prolonging the oxygen treatment period (Table III). The explanation at hand, *viz.* that phosphorus (a catalyst poison) is removed from the catalyst, is unlikely as the P/Pt ratio did not change appreciably. Probably the platinum complex decomposes but phosphorus remains bonded to the support in some way.

The high activity of the Pt/alumina catalysts prepared from the phosphine complex can be ascribed to the chemical nature of the interaction between the complex and the alumina surface, as suggested recently for other organometallic compounds and supports[3-5]. Tetrakis(triphenylphosphine)platinum thus suggests potentials in the preparation of Pt/alumina catalysts by means of bonded organo-complex compounds; this substance is advantageous by its relative stability during the time requisite for the impregnation. On the other hand, the high temperature of the oxidation treatment and reduction by hydrogen, necessary for the conversion. is a serious drawback making the compound unsuitable for the preparation of Pt/activated carbon catalysts.

LIST OF SYMBOLS

a_{max}	maximum adsorbed amount of platinum per unit weight of support (g/g)
a_{Pt}	adsorbed amount of platinum per unit weight of support (g/g)
A	outer surface area of support grain (mm^2)

c_i	concentration of platinum in catalyst calculated after the impregnation (%)
c_{Pt}	experimentally determined concentration of platinum in the catalyst (%)
C	concentration of platinum in the impregnating solution (g/dm^3)
C_e	equilibrium concentration of platinum in solution (g/dm^3)
r	radial coordinate of support grain (mm)
R	equivalent radius of catalyst grain, $R_e = 3\ V/A$ (mm)
t	period of impregnation (s)
V	volume of support grain (mm^3)

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