RELATION BETWEEN THE CONDITIONS OF PREPARATION AND THE ACTIVITY OF SUPPORTED PLATINUM CATALYSTS

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The preparation was studied of supported catalysts with different contents of platinum (0·21 to 9·25%) on activated carbon, suitable for liquid phase hydrogenations in mild conditions. The catalyst activity was tested in hydrogenations of nitrobenzene and 1-octene in ethanolic solutions at 25°C and atmospheric pressure of hydrogen. The highest specific activity was achieved by applying the following conditions: content of the active metal 0·5% Pt/C, calcination temperature 200°C, and temperature of the subsequent reduction with hydrogen 100°C.

Active metals of the platinum group can serve as catalysts in hydrogenation reactions[1]. Of these metals, particularly active are platinum and palladium, in the past applied usually in the form of metal black. Platinum black-based catalysts were prepared by reduction of platinum tetrachloride or chloroplatinic acid solutions[2,3]. Since platinum black is a rather expensive material, effort was made to devise supported platinum catalysts containing smaller amounts of platinum, which are less expensive and still exhibit activity comparable with that of Adam's catalysts[4]. In supported catalysts the content of the active component, usually platinum, exceeds 1% and in average is 1–10%. A separate group of supported platinum catalysts is reforming catalysts with contents of the active component not exceeding 0·5%. The properties of the catalysts depend markedly on the conditions of their preparation[5]. So, only if the effects of conditions are well understood, can the optimum conditions be adjusted so as to obtained a highly active catalyst with a relatively low content of the precious metal.

In the present work, platinum catalysts prepared by impregnation of activated carbon with chloroplatinic acid and its subsequent reduction with hydrogen were studied to seek how the conditions of preparation, namely, the temperatures of calcination and of reduction of the active component and the content of the latter, affect the catalyst activity in hydrogenation reactions.

EXPERIMENTAL

Chemicals. Hexachloroplatinic(IV) acid hexahydrate *p.a.* (Safina, Vestec). Ethanol denatured with 2% benzene (Spojené lihovary, Prague) and rectified before use, b.p. 78°C/98·2 kP; 96% azeotrope was used. Activated carbon Supersorbon (Degussa), extrudates 4 mm in dimater. Nitrobenzene *p.* (Lachema-Chemapol) distilled prior to use, b.p. 91°C/33 kPa. 1-Octene *p.*

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(Koch-Light) distilled prior to use, b.p. 119°C/101 kPa. 1-Mercaptobenzthiazole *p.a.* (Loba-Chemie). Hydrochloric acid *p.a.* (Lachema, Brno). Hydrogen peroxide *p.a.* (Chemické závody, Sokolov). Benzene *p.a.* (Lachema, Brno). Sodium sulphate anhydrous *p.a.* (Lachema, Brno). Phosphorus pentoxide *p.a.* (Lachema, Brno). Hydrogen, E grade, electrolytic (Technoplyn, Prague). Oxygen (unspecified, Technoplyn, Prague). Nitrogen for bulbs (Technoplyn, Prague). Helium min. 99·99% (Tega, Leipzig).

Catalyst preparation. The support was impregnated by circulating a solution of chloroplatinic acid over a fixed bed of activated carbon[6]. The impregnation was stopped when the concentration of the saturating solution dropped to zero or attained an equilibrium value. The saturated support was dried in a rotary vacuum evaporator, calcinated in an electric furnace in a stream of nitrogen ($4{\cdot}8\ \mathrm{dm}^3\ \mathrm{h}^{-1}$), and reduced with hydrogen ($6\ \mathrm{dm}^3\ \mathrm{h}^{-1}$) at 100—300°C. The time requisite for a proper calcination has been subject to investigation previously[7,8]. After the reduction, the catalyst was passivated at room temperature in a nitrogen stream for 12 h. The catalyst then was crushed into powder for activity measurements (below 50 μm) and for the determination of the platinum dispersity by hydrogen-oxygen titration (0·3—0·6 mm).

Measurement of the catalyst properties. The catalyst activity was determined as the initial rate of hydrogenation of nitrobenzene or 1-octene in ethanolic solution in a discontinuous stirred reactor at 25°C and atmospheric pressure of hydrogen. The apparatus and procedure were as described previously[9,10]. The dispersity of platinum metal within the catalyst was determined by two independent methods[11]: by X-ray diffraction (broadening of the Pt-111 line), and by hydrogen–oxygen titration. The radial concentration profiles of platinum across the catalyst grain were measured by electron microanalysis using a scanning electron microscope equipped with an analyzer of the X-ray dispersion (EDAX) (ref.[11]).

RESULTS AND DISCUSSION

Effect of Platinum Concentration

Usually, the first step in the preparation of supported catalysts is impregnation of the support with a solution of a compound of the active metal, which in the subsequent stages is calcinated and reduced. In this part of the study, the course of the impregnation of the support with solution of chloroplatinic acid in various concentrations was therefore examined in relation to the radial profile of platinum across a catalyst particle and to the sintering of the metal crystallites during the formation of the catalytically active surface, hence, during the calcination and reduction.

An example of the time dependence of the chloroplatinic acid concentration in the impregnation solution is shown in Fig. 1 for three different initial concentrations of the active component, resulting in different platinum contents in the catalyst. The time of impregnation, necessary for a complete adsorption of chloroplatinic acid, is seen to be proportional to its concentration[12]. The adsorption capacity of the activated carbon used is found to be very high.

The concentration of the impregnation solution affects the radial distribution of platinum across the catalyst particle. Fig. 2 shows the radial concentration profiles of platinum for three different metal concentrations. The majority of platinum was sorbed on the outer shell of the catalyst particle, where the maximum value was twice the mean content of platinum in the catalyst. The strong adsorption of chloroplatinic acid on activated carbon in aqueous medium thus results in a nonuniform distribution of platinum inside the catalyst. This effect is associated with the competitive adsorption of the active component and the solvent used on the surface of the support[11,13]. The high local concentration can bring about sintering of the platinum crystallites during the catalyst activation or during its operation at elevated temperature. This process affects the size of the crystallites of the active component, hence its specific surface area, and the catalyst activity.

The effect of the platinum content on its dispersity and activity is documented by Table I. The specific activity of catalysts prepared at 300°C decreases with increasing content of metal, while the mean diameter of the metal crystallites increases. The values of the latter measured by the two independent methods (by XRLB and by H—O titration) were in a good mutual agreement.

In view of the proportionality between the surface metal area and the consumption of adsorbate in the titration reaction, the dispersity of platinum can be characterized also simply in terms of the consumption of hydrogen (in normal conditions) required for a reaction with the chemisorbed oxygen; a direct relation can be also considered between the specific surface area of the active component and the catalyst activity.

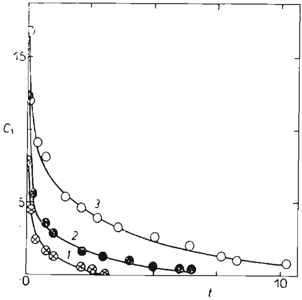

FIG. 1

Time dependence of the concentration of chloroplatinic acid in aqueous solution during the impregnation of activated carbon. Temperature 20°C, catalyst (% Pt/C): *1* 4·9, *2* 7·3, *3* 9·25

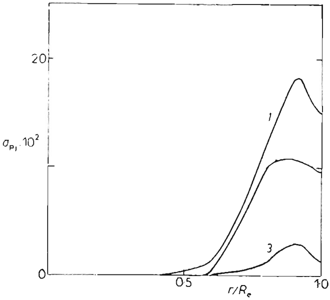

FIG. 2

Radial concentration profiles of platinum across the grain of catalysts with different contents of the active component (impregnation from water solution). Catalyst (% Pt/C): *1* 9·25, *2* 5, *3* 0·96

The dependence of the rate of the catalytic reaction on the dispersity of platinum thus can be expressed in the coordinates of Fig. 3, where the relation is depicted of the initial rate of hydrogenation of nitrobenzene or 1-octene to the volume of hydrogen taken up in the titration. The results can be regarded as a proof of a direct relation between the specific surface area of platinum and the hydrogenation activity of the catalyst.

TABLE I

Relation between the content of platinum in catalyst and the catalyst activity and platinum dispersity. Temperature of calcination and reduction 300°C

Platinum content in catalyst % (m/m)	Mean diameter of platinum crystallites nm		Activity mol H_2/kg_{Pt} s	
	d_{HOT}	d_{XRLB}	r_0(NB)	r_0(OEN)
0·96	9·6	13·1	4·31	3·01
2·45	10·4	17·7	2·76	2·52
4·90	17·2	19·0	1·87	1·49
7·30	17·6	20·2	1·40	1·04
9·25	25·9	28·3	1·29	1·29

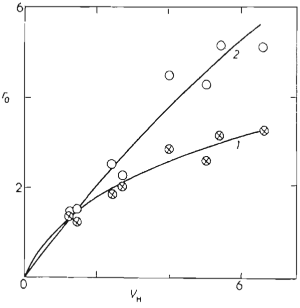

FIG. 3

Relation between the hydrogenation activity of the catalyst and the specific surface area of platinum. Hydrogenation of *1* nitrobenzene, *2* 1-octene

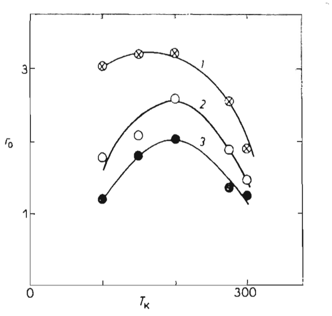

FIG. 4

Effect of the calcination temperature on the catalyst activity in the hydrogenation of nitrobenzene. Catalyst 9·25% Pt/C, reduction temperature (°C): *1* 100, *2* 200, *3* 300

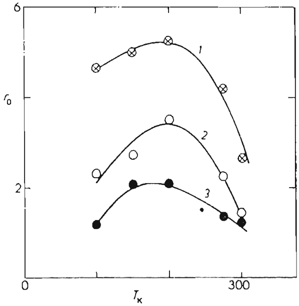

FIG. 5

Effect of the calcination temperature on the catalyst activity in the hydrogenation of 1-octene. Conditions as in Fig. 4

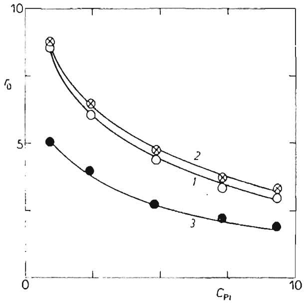

FIG. 6

Effect of the platinum content on the specific activity of the catalyst in the hydrogenation of nitrobenzene. Reduction temperature 100°C, calcination temperature (°C): *1* 100, *2* 200, *3* 300

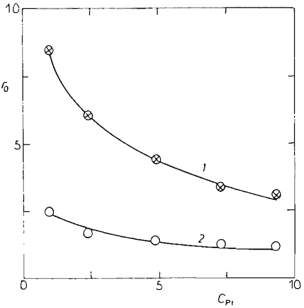

FIG. 7

Effect of the platinum content on the activity of the catalyst in the hydrogenation of nitrobenzene. Calcination temperature 100°C, reduction temperature (°C): *1* 100, *2* 300

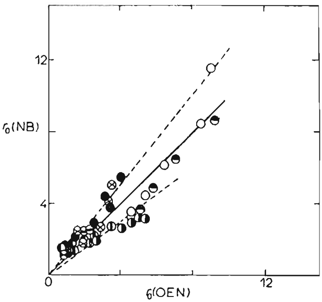

FIG. 8

Relation between the activities of the catalysts in hydrogenation of nitrobenzene and of 1-octene. Calcination temperature (°C) and reduction temperature (°C): ● 300, 300; ○ 100, 100; ⊘ 300, 100; ◐ 100, 300; ⊖ 200, 300; ◓ 200, 100; ◑ 100—300, 100; ⦶ 100—300, 200; ⊗ 100—300, 300

Effect of the Catalyst Preparation Temperature

There are two effects influencing the catalyst activity during the reduction of the active component coated on the support. First, higher temperatures favour a complete decomposition of the metal compound and desorption of the reduction products off the catalyst surface; a purre metal surface emerges and the process takes a shorter time. On the other hand, at higher temperatures the metal crystallites are sintered, which has an adverse effect on the specific surface area of the metal and thereby on the catalyst activity. Therefore, an optimum temperature (together with the corresponding reduction period) has to be sought for the catalyst preparation.

Moreover, the final activity of the catalyst is affected also by the calcination of the compound of the active component prior to its reduction. Catalysts with a platinum content of 9·25% (m/m) were prepared and calcinated at different temperatures, followed by reduction at one of the three preselected temperatures, 100, 200, or 300°C. For the hydrogenation of nitrobenzene and 1-octene, the relation between the catalyst activity and the temperature of calcination, for a given temperature of reduction, is shown in Figs 4 and 5, respecively. For each temperature of reduction an optimum temperature of calcination exists giving rise to the highest catalyst activity. Moreover, the lower was the reduction temperature, the higher catalyst activity emerged. Unfortunately, the time necessary for the reduction extends as the reduction temperature is lowered, so that a compromise must be chosen.

This applies also to catalysts with lower contents of the active component (Figs 6 and 7). The specific activity of the catalyst is found higher at lower contents of the active component, because the platinum crystallites are sintered to a lesser extent. As Fig. 8 demonstrates, there are no principal differences between the hydrogenation of nitrobenzene and of 1-octene; within ±25% a direct interdependence exists between the reaction rates of the two substances, so that the conclusions reached can be assumed to apply to both of them.

Based on the data of the present work, the following conditions can be regarded as optimum for the preparation of platinum-activated carbon catalysts: content of the active component 0·5% (m/m) Pt/C, temperature of calcination 200°C, temperature of reduction with hydrogen 100°C.

As to the calcination of chloroplatinic acid, compounds are conceived[14] to be formed in which platinum is in a lower oxidation state, so that the catalyst preparation at different temperatures can be looked upon as reduction of different platinum compounds. The effect of the nature of the starting compound of the active component on the forming of the final catalytically active surface will be subject to further investigation.

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LIST OF SYMBOLS

C_0	initial concentration of the active component in solution (mol l^{-1})
C_1	initial concentration of chloroplatinic acid in solution (kg m^{-3})
C_{Pt}	concentration of platinum in catalyst (% (m/m))
d	mean diameter of platinum crystallites calculated as average of d_{HOT} and d_{XRLB} (nm)
d_{HOT}	mean diameter of platinum crystallites determined by H—O titration (nm)
d_{XRLB}	mean diameter of platinum crystallites determined by X-ray investigation (nm)
r_0	initial rate of hydrogenation (mol H_2/kg_{Pt} s)
r_0(NB)	initial rate of hydrogenation of nitrobenzene (mol H_2/kg_{Pt} s)
r_0(OEN)	initial rate of hydrogenation of 1-octene (mol H_2/kg_{Pt} s)
t	time (S)
T	temperature (°C)
T_r	temperature of catalyst reduction (°C)
T_c	temperature of catalyst calcination (°C)
V_H	volume of hydrogen taken up in the titration of the platinum surface (ml/g)

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