

PREPARATION OF A PLATINUM CATALYST ON CHARCOAL BY REDUCTION OF CHLOROPLATINIC ACID WITH HYDROGEN

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The purpose of this work was to investigate the effect of preparation conditions on the activity of catalysts containing 5% (w/w) of platinum on charcoal, obtained by reduction of chloroplatinic acid with hydrogen. Knowledge of this effect makes it possible to choose the optimum conditions and prepare highly active catalysts with a relatively low content of the active component. Our attention was focussed on the kinetics of the reduction of chloroplatinic acid (on charcoal as support), followed by measuring the content of hydrogen chloride and chlorine in the reduction outlet gas.

A number of methods for preparation of platinum catalysts have been advanced; a detailed review of the literature was given previously¹. In that paper we dealt with catalysts on charcoal containing from 2.5 to 15% (w/w) of platinum and compared them with the Adams catalysts². The preparation of a platinum catalyst on charcoal consists of several operations, discussed further.

Saturation of the support by the active component. The active components most frequently employed are chloroplatinic acid^{1,3-7} and the Riesel chloride^{3,5,8}, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. The support is generally in a granulated form, so that the question arises whether the active component penetrates a whole granule evenly^{6,9}. The amount of the adsorbed chloroplatinic acid was found³ to depend markedly on the quality of the support; the authors believe that the active centres of charcoal have the character of an electron acceptor, thus explaining the much better adsorption of the anions PtCl_6^{2-} as against that of the cations $\text{Pt}(\text{NH}_3)_4^{2+}$. It was also reported^{3,6} that sorption of chloroplatinic acid on charcoal and on γ -alumina proceeds by different mechanisms. The solvents used for saturation of a support are lower ketones¹⁰, electron-donating solvents¹¹ and deionized water¹².

Drying of support saturated with an active component. A saturated support is usually dried in the air at 100–130°C for several hours^{1,3,4,9,13}. The literature gives some information how the way of drying a saturated support influences the final catalytic activity of the catalyst.

Reduction and passivation of a catalyst. An active component on the support is normally reduced in a flow of hydrogen for 2 or more hours^{1,3,5,9,13}. The optimum conditions of the reduction, leading to highest activity of the catalyst, have been found to vary in a considerable range, depending mainly on the quality of the support and the starting compound of platinum. After the reduction the catalyst is passivated in a flow of cold nitrogen for a few hours⁹. In the passiva-

tion hydrogen desorbs from the surface of the catalyst whereby the pyrophoric property of the latter is extinguished.

EXPERIMENTAL

Chemicals

Ethanol (denatured with 1% of methanol, Spojené lihovary, Prague) was rectified before use; b.p. 78°C/98.06 kPa. 2-Methyl-3-buten-2-ol (pure, Koch-Light Laboratories, Colnbrook) was rectified prior to use; b.p. 97°C/98.06 kPa. Nitrobenzene (A.G., Lachema Chemapol, Prague) was also rectified before use; b.p. 79°C/1.07 kPa. Platinum tetrachloride was prepared by pyrolysis of chloroplatinic acid in streaming chlorine¹⁴. Also employed were: silver nitrate (A.G., Safina, Vestec), sodium bicarbonate (pure), sodium hydroxide (A.G.), sodium chloride (A.G.), potassium chromate (A.G.), potassium iodide (A.G.), (all Lachema, Brno); chloroplatinic acid hexahydrate (A.G., Safina, Vestec), acetic acid (A.G.), sodium thiosulphate (A.G.), (all Lachema, Brno); Filament-lamp nitrogen (MCHZ, Ostrava), hydrogen (technical, grade B, and electrolytic, Technoplyn, Pardubice), charcoal (Supersorbon, Degussa, G.F.R.) grade H8-3, pellet size 3–4 mm, bulk density 350 kg/m³, water content 8%, ash content 2%, volume of pores 70%, specific surface 1200 m²/g.

Preparation of the Catalyst

Pellets of charcoal (95 g) were poured, as one portion, to a distilling flask that had been charged with chloroplatinic acid hexahydrate (13.27 g) dissolved in distilled water. The support was saturated with the solution under stirring for 1 h. The excess of water was then evaporated on a rotary vacuum evaporator (bath temperature 55°C). The support, saturated with chloroplatinic acid, was dried at a pressure of 1.33 kPa and a temperature of 65°C for 8 h. All catalysts were prepared from one batch of the saturated support. A stationary bed of the granulated, saturated and dried support (5 g) was pyrolysed and reduced in a glass tube (I.D. 25 mm) heated by an electric mantle. After flushing the tube with nitrogen for 20 min (flow rate 80 cm³/min) the tube (reduction furnace) was brought to a selected temperature and chloroplatinic acid on the carbon support was pyrolysed in the flow of nitrogen (catalysts KI). The pyrolysis was allowed to proceed until the gas leaving the tube was practically free of hydrogen chloride. The nitrogen was then replaced by hydrogen (flow rate 100 cm³/min) and the catalyst was reduced until no hydrogen chloride was detected in the gas. Then hydrogen was replaced by cool nitrogen (80 cm³ per min) in which the catalyst was passivated for at least 12 h.

With catalysts KII the reduction furnace was brought to a selected temperature, then nitrogen was immediately replaced by hydrogen and the reduction started. When the reduction was finished the catalysts were passivated in the same way.

The passivated catalysts were crushed to a grain size below 0.063 mm.

Gas Analysis

The gases leaving the reduction furnace passed in the counter-current way through an absorption column, represented by a glass tube, I.D. 20 mm, packed to a height of 100 mm with tiny stainless-steel spirals, diameter 2 mm. The solution of hydrogen chloride, absorbed in distilled water, was analysed according to Mohr¹⁵. In simultaneous determination of chlorine and hydrogen chloride the reduction outlet gases were absorbed in 0.1M sodium hydroxide. Hypochlorites and chlorides were determined titrimetrically (refs^{16,17} and ¹⁵, respectively).

Determination of Catalytic Activity

The catalysts were tested in a discontinual, thoroughly stirred reactor¹⁸ at 25°C and atmospheric pressure. The model substrates were nitrobenzene and 2-methyl-3-buten-2-ol in ethanol as solvent. In the arrangement described the hydrogenation occurred, from the viewpoint of a mass transport, in the kinetic region¹⁹. The effect of internal diffusion was eliminated by sufficient graining of the catalyst (particle size ≤ 0.063 mm). A measure of the catalytic activity was the rate constant in the equation for the hydrogenation rate²⁰, which is first order in respect to hydrogen concentration and zero order to the substrate. The rate constants of hydrogenation refer to a hydrogen pressure of 0.1013 MPa (the calculations were corrected for solvent vapour tension²¹ and change in atmospheric pressure).

RESULTS AND DISCUSSION

Pyrolysis and Reduction of the Platinum Compounds

Pyrolysis of chloroplatinic acid at too high temperatures may liberate free chlorine, which might impair the activity of the catalysts. For this reason we investigated the course of the decomposition. Free (not bound to the support) chloroplatinic acid was thermally decomposed^{22,23} in streaming nitrogen, then reduced with hydrogen while the quantities of the released hydrogen chloride and chlorine were measured in relation to temperature and time. The course of the decomposition in relation to temperature is given in Fig. 1. The free chloroplatinic acid was thermally de-

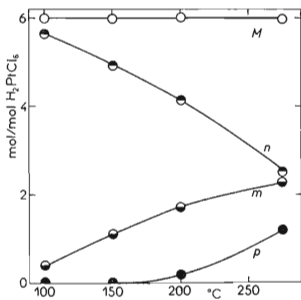


FIG. 1

Pyrolysis and Reduction of Chloroplatinic Acid in Relation to Temperature

M total chlorine, *m* hydrogen chloride (pyrolysis), *n* hydrogen chloride (reduction) *p* free chlorine (pyrolysis).

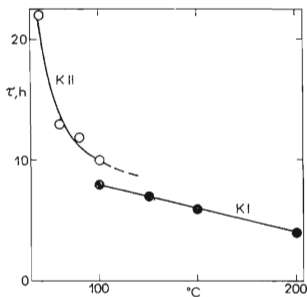
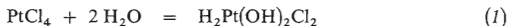


FIG. 2

Reduction Times of the Catalysts in Relation to Temperature of the Reduction

composed and reduced for the same time as the catalysts (Fig. 2) and the other experimental conditions were also identical with those used in the preparation of the catalysts.

The results in Fig. 1 show that the reduction time of chloroplatinic acid at the given temperatures was sufficient for the reduction to metallic platinum to be complete (see the total quantities of the determined chlorine). At 275°C one mol of chloroplatinic acid gave more than 2 mol of hydrogen chloride, which is not consistent with the assumed decomposition to platinum tetrachloride. Part of platinum tetrachloride evidently combined with the crystal water of chloroplatinic acid, *e.g.*



This compound, mentioned in the literature^{14,22} may decompose further with the formation of more hydrogen chloride. Another part of platinum tetrachloride, exposed to a high temperature, gets converted to lower chlorides of platinum with the simultaneous liberation of elemental chlorine²² (Fig. 1).

Pyrolysis of platinum tetrachloride should theoretically give elemental chlorine only. At 275°C, however, a considerable amount of hydrogen chloride evolved (0.065 mol per mol of PtCl_4). We suppose that in handling the hygroscopic platinum tetrachloride some aerial moisture got absorbed and the decomposition was then analogous to that of chloroplatinic acid.

Pyrolysis and Reduction of Chloroplatinic Acid on Charcoal

The catalysts, containing 5% (w/w) of Pt on charcoal, were divided according to mode of preparation into two groups, *viz.* KI and KII. In preparing the catalysts we followed the effect of the reduction temperature on their final activity and on the total amount of the hydrogen chloride liberated.

The effect of reduction temperature on the catalytic activity was investigated in a range of 70–200°C. The reduction was allowed to proceed until it was complete at a selected temperature, so that the catalysts could be compared. Fig. 2 illustrates the temperature dependence of time necessary for complete reduction of a catalyst. The dependence of activity of the catalysts KI and KII upon temperature of the reduction is shown in Fig 3; it is seen that at lower temperatures highly active catalysts were formed.

The total amount of hydrogen chloride liberated in the preparation of a catalyst was found to increase with increasing temperature of the reduction, despite the fact that the reduction was allowed to proceed until the gas leaving the tube no longer contained hydrogen chloride. Pyrolysis and reduction of 1 mol of chloroplatinic acid should theoretically give 6 mol of hydrogen chloride; the real quantities were invariably lower (Fig. 4). Hence it can be judged that a part of the liberated hydrogen

chloride remains adsorbed on the catalyst. Fig. 4 further shows that pyrolysis at temperatures above 100°C gave more hydrogen chloride than would be consistent with stoichiometry.

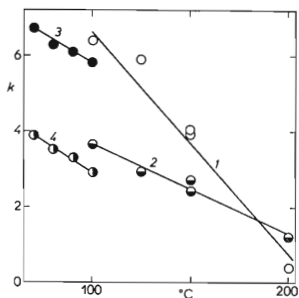


FIG. 3

Activity of the Catalysts in Reaction to Temperature of the Reduction

1 KI (hydrogenation of 2-methyl-2-buten-2-ol), 2 KI (hydrogenation of nitrobenzene), 3 KII (hydrogenation of 2-methyl-3-buten-2-ol), 4 KII (hydrogenation of nitrobenzene).

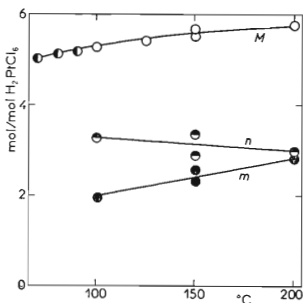


FIG. 4

Liberated Hydrogen Chloride in Relation to Temperature

○ *M* Total amount of liberated chlorine (catalysts KI), ● *M* total amount of liberated chlorine (catalysts KII), ● *m* hydrogen chloride (pyrolysis), ● *n* hydrogen chloride (reduction).

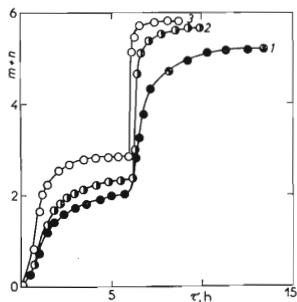


FIG. 5

Pyrolysis and Reduction of Catalysts KI
1 100°C, 2 150°C, 3 200°C.

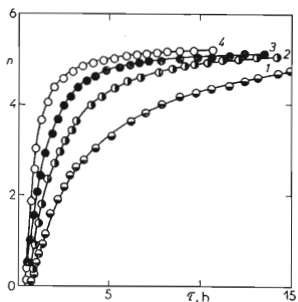


FIG. 6

Reduction of Catalysts KII
1 70°C, 2 80°C, 3 90°C, 4 100°C.

In preparing catalysts KI chloroplatinic acid on charcoal was first pyrolysed in streaming nitrogen. The reaction intermediate, essentially platinum tetrachloride on charcoal (Fig. 5), was then reduced in streaming hydrogen. From the time course of the reduction the apparent reaction order of the reduction in respect to platinum tetrachloride was assessed as approximately equalling 2. From the initial reduction rates we also determined the activation energy of reduction of platinum tetrachloride on active carbon as 26.2 kJ/mol.

Catalysts KII were prepared under conditions securing that no pyrolysis of chloroplatinic acid coating the carbon support could possibly occur. The reduction rate was studied in a range of 70–100°C. The time sources of the reduction rates (Fig. 6) were evaluated as in the preceding case. The apparent reaction order of the reduction in respect to chloroplatinic acid was 1.5. From the initial rates of reduction of chloroplatinic acid by hydrogen we further determined the apparent activation energy of reduction of chloroplatinic acid on active carbon as (63.2 kJ/mol).

Of all the experiments in which chloroplatinic acid on charcoal was pyrolysed and reduced, elemental chlorine leaving the reduction furnace was detected in none. No chlorine was detected even in heating the support that had been soaked in a solution of platinum tetrachloride. We find this fact difficult to explain. Either chlorine is liberated but strongly adsorbed by the support, or the platinum compounds decompose in some other way.

LIST OF SYMBOLS

k	rate constant of hydrogenation	(mol H ₂ kg _{cat} ⁻¹ s ⁻¹)
M	the total amount of liberated chlorine (Cl ₂ + HCl) in the preparation of a catalyst	(mol Cl per mol H ₂ PtCl ₆)
m	hydrogen chloride liberated by pyrolysis	(mol HCl per mol H ₂ PtCl ₆)
n	hydrogen chloride liberated by reduction	(mol HCl per mol H ₂ PtCl ₆)
p	elemental chlorine liberated by pyrolysis	(mol Cl ₂ per mol H ₂ PtCl ₆)
t	temperature	(°C)
τ	time of reduction or pyrolysis	(h)

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