THE EFFECT OF PREPARATION CONDITIONS OF A PLATINUM HYDROGENATION CATALYST ON ITS ACTIVITY AND ON THE DISPERSITY OF PLATINUM CRYSTALLITES

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The paper deals with the preparation of a hydrogenation catalyst, 5% of platinum on active carbon. The support was saturated with aqueous chloroplatinic acid or platinum tetrachloride. After calcination in streaming nitrogen the catalyst was reduced with hydrogen. We studied the effects of temperatures of the calcination and the reduction on *1)* the formation of hydrogen chloride in the course of calcination and the following reduction, *2)* the dispersity of metallic platinum and 3) the catalytic activity for hydrogenation of 2-methyl-3-butene-2-ol and nitrobenzene in liquid phase. The catalytic activity was found to be proportional to the dispersity of platinum.

The platinum-on-support catalysts with 5 to 10% (w/w) platinum, have found rather widespread use in technology of organic compounds for hydrogenation of double bonds and aromatic nitro groups, for some hydrogenolytic reactions, *etc.* The literature gives information on various preparation method and on properties of these catalysts[1,2], but many papers lack quantitative data on the optimum conditions for the preparation of a catalyst. Our preceding paper[3] described reduction of hexachloroplatinic acid with hydrogen, dealing especially with the effect of temperature at which a catalyst is prepared on its activity for hydrogenation of 2-methyl-3-butene-2-ol and/or nitrobenzene in ethanol under atmospheric pressure. The properties of the catalysts proved considerably dependent on temperatures of their calcination and reduction.

The purpose of the present paper was to justify our assumption that at low temperatures the catalysts exhibit a higher dispersity of the metallic platinum produced by the reduction, so that the activity of such catalysts is higher.

EXPERIMENTAL

Chemicals. Chloroplatinic acid, A.G., (Safina, Nat. Corp., Vestec); platinum tetrachloride was obtained[4] by heating chloroplatinic acid in a stream of chlorine (Spolana, Neratovice); active carbon Supersorbon HB-3 (Degussa, F. R. G.), pellet diameter 3—4 mm; technical electrolytic hydrogen B (Technoplyn, Pardubice); bulb nitrogen (MCHZ, Ostrava); ethanol with 1% of methanol, rectified before use (Spojené lihovary, Prague); 2-methyl-3-butene -2-ol, pure (Koch-Light Lab., Colnbrook), rectified before use, b.p. 97°C/98·06 kPa; nitrobenzene, A.G., (Lachema-

-Chemapol, Prague), rectified before use, b.p. 79°C/1·07 kPa. For further details on the chemicals used see the preceding paper[3].

Catalysts. The principle of their preparation was described previously[3]. The pellets of active carbon were soaked with an aqueous solution of the platinum compound (catalysts KI-H_2PtCl_6, catalysts K II-$PtCl_4$) for 1 h. After drying the saturated support in a rotary vacuum evaporator at 60°C the pellets were placed into an electric oven where the catalyst was calcinated at a chosen temperature (100—275°C) in streaming nitrogen until evolution of hydrogen chloride had ceased (the gas was analysed by Mohr's method[3,5]). The needed times of calcination are given in the previous paper[3], wherein we also pointed out that neither calcination nor reduction was accompanied by evolution of chlorine. The course of the following reduction with hydrogen (at the same temperature) was also monitored by evolution of hydrogen chloride. After the reduction had ended the catalyst was passivated in a stream of nitrogen and the pellets were crushed and sieved on a mesh. The catalytic activity was measured with a fraction of mesh 0·063 mm.

Measurement of catalytic activity. The activity of a catalyst was determined by hydrogenation of 1 ml of 2-methyl-3-butene-2-ol or nitrobenzene in 25 ml of ethanol under atmospheric pressure at 25°C. The reaction was of zero order with respect to either substrate. A measure of the catalytic activity was the rate constant of hydrogenation. The apparatus and procedure were described previously[6,7].

RESULTS AND DISCUSSION

Calcination and reduction of a catalyst. As was previously found[3], the temperature at which a catalyst was prepared has a considerable effect on pyrolysis and reduction of the platinum compound and on the resulting activity of the catalyst.

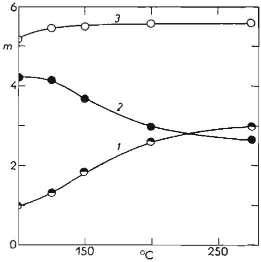

FIG. 1

Amount of Hydrogen Chloride m (mol/mol) Related in Preparation of Catalysts K I from H_2PtCl_6 at Different Temperatures

1 Calcination of H_2PtCl_6 in a stream of nitrogen, 2 reduction with hydrogen, 3 total amount.

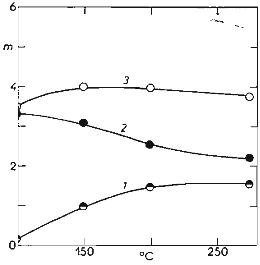

FIG. 2

Amount of Hydrogen Chloride Released in Preparation of Catalysts K II from $PtCl_4$ at Different Temperatures

1 Calcination of $PtCl_4$ in a stream of nitrogen, 2 reduction with hydrogen, 3 total amount.

Figs 1 and 2 show that calcination at higher temperatures brought about reaction of the platinum compound (chloroplatinic acid in Fig. 1 and platinum tetrachloride in Fig. 2) with the water, sorbed on the support, which was used as solvent in saturation of the support with the active component. At the higher temperatures of calcination the catalyst K I liberated more hydrogen chloride than would correspond to stoichiometry of the reaction (Fig. 1):

$$H_2PtCl_6 \rightarrow PtCl_4 + 2\,HCl \tag{1}$$

The reaction of chloroplatinic acid with water obviously is

$$H_2PtCl_6 + 2\,H_2O \rightarrow H_2Pt(OH)_2Cl_4 + 2\,HCl\,, \tag{2}$$

The formed dihydroxytetrachloroplatinic acid may undergo the subsequent decomposition

$$H_2Pt(OH)_2Cl_4 \rightarrow Pt(OH)_2Cl_2 + 2\,HCl\,. \tag{3}$$

Platinum tetrachloride reacts analogously with water (Fig. 2)

$$PtCl_4 + 2\,H_2O \rightarrow H_2Pt(OH)_2Cl_4\,. \tag{4}$$

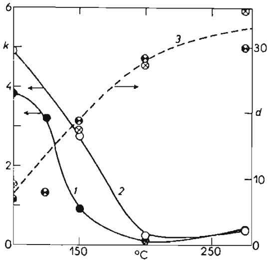

FIG. 3

Effect of Preparation Temperature of a Catalyst on the Rate Constant of Hydrogenation of 2-methyl-3-butene-2-ol ($m^3\,min^{-1}\,.\,kg^{-1}$) and on the Mean Size of Platinum Crystallites (nm)

1 Catalysts K I (H_2PtCl_6), *2* catalysts K II ($PtCl_4$), *3* size of platinum crystallites. ⊖ K I, ⊗ K II.

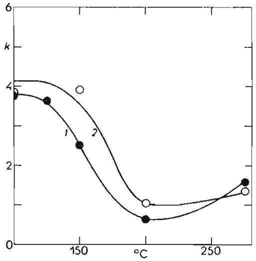

FIG. 4

Effect of Preparation Temperature of a Catalyst on the Rate Constant of Hydrogenation of Nitrobenzene ($m^3\,min^{-1}\,kg^{-1}$)

1 Catalysts K I (H_2PtCl_6), *2* catalysts K II ($PtCl_4$).

Activity of the catalysts. Figs 3 and 4 show the hydrogenation rate constants of 2-methyl-3-butene-2-ol and nitrobenzene, respectively, in relation to the temperatures at which the catalysts K I and K II were prepared. It is apparent from either figure that lower temperatures gave rise to more active catalysts. Further it is evident that the catalysts K II, prepared from platinum tetrachloride, were more active than the catalysts K I, preparared from chloroplatinic acid. Consequently, the main result of this work is the discovery that such conditions as produce slow calcination and slow reduction (at temperatures not exceeding 100°C) are optimum for preparation of the most active catalysts. We assumed that under these conditions small crystallites of metallic platinum were formed on the surface of the catalyst support, with a very large specific surface of the active component on the support as a result. This hypothesis was substantiated by measuring the mean diameter of the crystallites (see the dashed line in Fig. 3) by the method[8-11] of extending the X-ray diffraction line Pt (111), using a diffractometer Geigerflex D-6-C with a goniometer S6-7 of the firm Rigaku Denki, Ltd. (Japan).

Dispersity of platinum. Fig. 5 shows linear relations between the rate constant of hydrogenation of 2-methyl-3-butene-2-ol and dispersity of platinum in the catalysts K I and K II. With the hydrogenation of nitrobenzene this relation was not a linear one (Fig. 6). The activity of catalysts with a high dispersity of platinum was little dependent on conditions of their preparation. In this case it was also rather immaterial which platinum compound was used to prepare the catalysts.

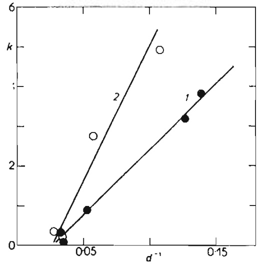

FIG. 5

Activity of Catalysts for Hydrogenation of 2-Methyl-3-butene-2-ol in Relation to Dispersity of Platinum

1 Catalysts K I (H_2PtCl_6), 2 catalysts K II ($PtCl_4$).

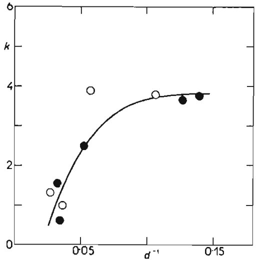

FIG. 6

Activity of Catalysts for Hydrogenation of Nitrobenzene in Relation to Dispersity of Platinum

● Catalysts K I (H_2PtCl_6), ○ catalysts K II ($PtCl_4$).

Figs 5 and 6 indicate that the hydrogenation mechanismus of 2-methyl-3-butene-2-ol and nitrobenzene are different. However, with hydrogenation in the liquid phase the experimental findings do not allow us to draw any safe conclusions on the mechanisms of sorption and the surface reaction on the catalysts, as the surface phenomena may be affected by adsorption of the solvent.

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