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NOTES

Determination of the Distribution of the Active Component and the Activity of Supported Palladium Catalysts

This article reports a novel way of determining the distribution of an active component (Pd) on a carrier (active carbon). Preliminary tests have shown that the method may be used also for other platinum metals and other carriers. The principle of the method (*1*) is that grains of palladium carrier catalysts or some suitable chosen parts of them are used in the catalytic decomposition of copper (II) formate in an aqueous solution. Copper separates on the sites of the active component, while the carrier remains intact. An electron microdetector was used to verify this fact. Sites covered with copper can be readily located optically because they always differ in color from the carrier. The rate of decomposition of copper (II) formate, obtained by measuring the rate of release of copper or the rate of evolution of gases, is proportional to the activity of the catalyst used.

The method permits the investigation of preparative procedures which affect the distribution of the active component and the activity of catalysts, and may therefore be utilized in optimizing the preparation of catalysts.

Formic acid decomposition is most frequently catalyzed by metals or their oxides, and Mars *et al.* (*2*) have reviewed the decompositions of formic acid and metal formates. Temperatures higher than those given in this work are normally employed, and use of the decomposition reaction for the purpose described in this article has not yet been given in the literature.

EXPERIMENTAL

Catalysts with an approximate content of 3% Pd on active carbon were used, either in granular form as cylinders, 4 mm in diameter, 7–8 mm long, or pulverized, with mesh fraction ≤0.063 mm. The carrier was saturated with a solution of palladium chloride at 20°C and atmospheric pressure with stirring. Each time 10 g of active carbon in granular or pulverized form was used, together with 100 ml of a solution of $PdCl_2$ (1.27 ml of 40% solution of $PdCl_2$, completed with water to 100 ml). Catalysts possessing various distributions of the active component were obtained by taking samples of grains at suitable time intervals, drying them at 90–100°C, and reducing with hydrogen. In the case of powder catalysts, water was evaporated on a rotary vacuum evaporator after completion of saturation (50 min), and the catalysts were dried at 90–100°C for 6 hr.

The catalysts in granular form were reduced in a stationary bed at 150°C for 1 hr. The reactor was flushed with nitrogen before and after the reduction. Powder catalysts were reduced in an electrically heated reduction oven at 150°C (C1) or 270°C (C2). The reduction time was 460 min, and the catalysts were stirred during the reduction in order to achieve homogeneity. Some catalysts were washed four times, each time by stirring in 100 ml of water and sedimentation (C1-W, C2-W). The catalysts were then dried at 90–100°C to constant weight.

A commercial catalyst, Cherox 41-00 (CHZ ČSSP Záluží, Czechoslovakia), was also used, either in granular or in powder form. In this case $PdCl_2$ was reduced to Pd using formaldehyde.

A stirred vessel was used for the decomposition. Two-hundred milliliters of a 1% aqueous copper (II) formate and 1.2 g of pulverized catalysts were used; the temper-

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FIG. 1. Longitudinal cross section through catalyst grain (Cherox 41-00) with separated copper (decomposition time 4 min). Magnified 10×.

ature was 20°C. Samples ca. 2 ml in volume were taken for the colorimetric determination. The catalysts were quickly removed by centrifugation and the samples were analyzed.

The hydrogenation activity was measured with a standard testing apparatus (*3*) by measuring the rate of hydrogenation of 1-hexene in a toluene solution under normal conditions.

RESULTS AND DISCUSSION

Determination of the Distribution of the Active Component

Gas analysis showed that the decomposition of the aqueous copper (II) formate proceeded predominantly according to the equation

$$Cu(OOCH)_2 \rightarrow Cu + H_2 + 2CO_2.$$

Carbon monoxide was detected in trace amounts only; the mixture consisted virtually of 68% CO_2 and 32% H_2.

The micrographs in Figs. 1 and 2, which show the longitudinal and transverse cross sections of a catalyst grain with released copper, document the suitability of this method for a preliminary determination of the distribution of the active component of the supported catalyst. Localization of the released copper makes it possible to estimate the distribution of palladium. The

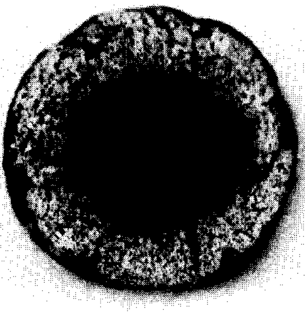

FIG. 2. Transverse cross section through catalyst grain (Cherox 41-00) with separated copper (decomposition time 4 min). Magnified 10×.

TABLE 1

Rate of Penetration of Solution of Copper (II) Formate into the Catalyst Grain

Time (s)	Radius of transverse cross section a (cm)	Distance of boundary Cu-carrier from the center of transverse cross section r (cm)	Penetration coefficient D(cm^2/s) × 10^6
300	0.29	0.25	4.0
600	0.29	0.23	4.5
1200	0.30	0.21	5.1
1800	0.27	0.14	6.8
3000	0.28	0.08	9.7
3600	0.28	0.07	9.2

method is advantageous because of its simplicity and quickness.

The rate of penetration of a solution of palladium chloride inside the carrier was determined from a series of grain samples with various saturation times. After drying and reduction with hydrogen, the grains were divided by means of transverse cuts and used in the decomposition of copper (II) formate. The cross sections were photographed, and enlarged micrographs were used to measure distances between the boundaries and the centers of circular transverse cuts. The penetration coefficient, D, was calculated using relationships for the rate of diffusion in an infinite cylinder (*4*). The measured and calculated values are summarized in Table 1. The diffusion coefficients of salts (KCl, $CaCl_2$, $BaCl_2$) in water at 25°C vary (*5, 6*) from 1–2 × 10^{-5} cm^2/s. The effective diffusion coefficient in the porous structure of the catalyst is smaller by approximately one order of magnitude than that of molecular diffusion (*7*). The process of penetration of palladium chloride in an aqueous solution into an originally dry particle is very complicated. Since the liquid is not degassed, air must be squeezed out from the pores, the liquid undergoes capillary rise in the pores of the carrier, and molecules of palladium chloride are trapped on the carrier. The measured average penetration coefficient, $D = 8 \times 10^{-6}$ cm^2/s, which reflects these influences, seems to be real.

Determination of the Activity of Supported Palladium Catalysts

The activity of the catalysts may be measured by the rate of decomposition of copper (II) formate. The rate of decomposition of copper (II) formate can be expressed as the rate of copper separation on palladium sites, of the rate of loss of copper (II) formate in an aqueous solution, or of the rate of evolution of hydrogen and carbon dioxide. Quantitative data are best obtained by a colorimetric investigation of the drop in the concentration of copper (II) formate on the basis of a change in color of the aqueous solution during the decomposition.

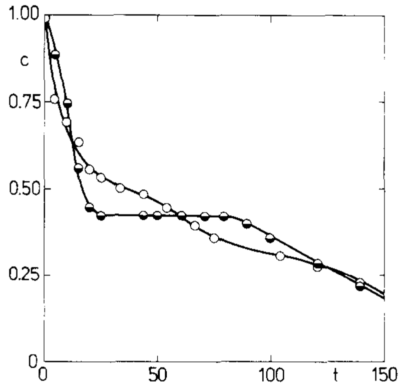

FIG. 3. Time dependence of concentration of copper (II) formate in solution during decomposition on catalysts reduced with formaldehyde (Cherox 41-00). ◒, normal course; ○, hydrogen was introduced into the beaker during decomposition (activation of the catalyst); *c*, dimensionless concentration (instantaneous concentration related to the initial one); *t*, time (min).

Figure 3 shows the decrease in concentration of copper (II) formate as a function of time. Catalyst reduced the formaldehyde has a plateau on the concentration curve, during which there were no visible changes in the concentration of copper (II) formate in solution. This plateau virtually disappeared after activation of the same catalyst with hydrogen during the decomposition; with catalysts prepared by reduction with hydrogen, there was no plateau at all (cf. Fig. 4). The plateau is obviously due to the deficiency of hydrogen dissolved in palladium. The initial steep decrease in concentration of copper (II) formate is due to its sorption on active carbon. A virtually identical dependence within the concentration range $c = 1$ to $c = 0.63$ was measured with the carrier alone; here, however, concentration decreased no more after reaching $c = 0.63$.

Figure 4 shows the effect of the temperature of reduction on the activity of palladium catalysts reduced with hydrogen. A temperature of 270°C is already too high, and the catalyst reduced at this temperature is much less active than that reduced at 150°C. This finding agrees with that on the effect of the temperature of reduction on the activity of palladium catalysts in the dehydrogenation of 2-ethoxycyclohexanol to 2-ethoxyphenol (*8*).

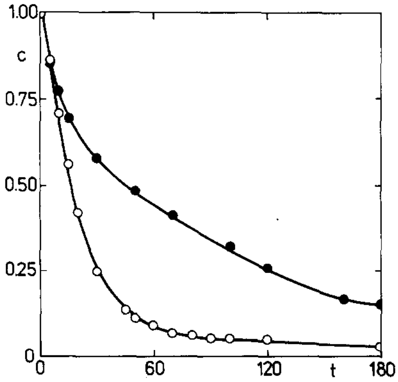

FIG. 4. Time dependence of concentration of copper (II) formate in solution during decomposition on catalysts reduced with hydrogen. ○, C1-reduction temperature 150°C; ●, C2-reduction temperature 270°C.

TABLE 2

Rate of Hydrogenation of 1-Hexene and Rate of Decomposition of Copper (II) Formate on Palladium Catalysts

Catalyst	Rate of hydrogenation (ml $H_2\,g_{cat}^{-1}\,min^{-1}$)	Rate of decomposition ($g_{(HCOO)_2Cu}\,g_{cat}^{-1}\,min^{-1}$) × 10^3
C1	350	47
C1-W	17	26
C2	65	7
C2-W	60	1.3
Cherox 41-00	55	6

Table 2 summarizes the rates of hydrogenation of 1-hexene and decomposition of copper (II) formate, measured by means of selected powdered catalysts. The rate of hydrogenation was constant in all cases within a broad time interval. For a quantitative comparison, tangent lines were constructed at the point $c = 0.63$ of the colorimetric curves. These tangent lines gave the rate of decomposition of copper (II) formate in a range where the sorption conditions on the catalyst had already been established. For the catalyst reduced with formaldehyde (Cherox 41-00), when the whole process is much more complicated, the rate of decomposition was determined only in the region beyond the plateau ($c = 0.42$), that is, at a lower initial concentration of copper (II) formate.

It can be clearly seen from Table 2 that the rates of decomposition are related to the rates of hydrogenation. The largest anomaly was exhibited by the catalyst C2-W, where the rate of decomposition was markedly lower compared with the others.

Further research will be concentrated on a more detailed kinetic study of the decomposition process itself and on further possibilities of utilizing this reaction in the study of preparation and properties of supported catalysts of the platinum metals.

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L. ČERVENÝ
A. MARHOUL
K. ČERVINKA
V. RŮŽIČKA

Department of Organic Technology
Prague Institute of Chemical Technology
Suchbátarova 5, Prague 6,
Czechoslovakia

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