THE USE OF CATALYZED DECOMPOSITION OF CUPRIC FORMATE FOR STUDY OF PROPERTIES OF PALLADIUM CATALYSTS

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The decomposition of cupric formate induced by palladium catalysts has been studied in aqueous solution. Effects of the carrier and the proper active component on the cupric formate concentration decrease have been separated. Kinetic data of the decomposition reaction have been obtained, and processes affecting the decomposition have been followed. The decomposition rates found with the use of various catalysts enabled to test the effects of preparation methods of palladium catalysts on their activity. The values found agree with hydrogenation activity of the catalysts.

The decomposition of cupric formate in aqueous solution at room temperature induced by the catalysts based on metals of the VIII[th] group makes it possible to obtain valuable information about these catalysts[1,2]. A survey of reactions of formic acid and its salts is given in ref.[3], however the catalyzed decompositions were only followed at higher temperatures for other purposes. The decomposition on palladium catalysts proceeds[2] according to the equation:

$$(HCO_2)_2Cu \rightarrow Cu + H_2 + 2\,CO_2\,, \qquad (I)$$

copper being deposited at the sites of the active component, which enables its optical localization[1,2] and, hence, determination of the active component on the carrier.

Rate measurement of the catalyzed decomposition, which can easily be carried out *e.g.* colourimetrically, presents thus valuable information about activity of the catalyst used.

Study of factors influencing the course of cupric formate decomposition enables, on the one hand, modification and optimization of preparation of the metal catalysts, and, on the other hand, it can contribute to general theory of action of these catalysts in other reactions, too. These aspects are dealt with in the present communication.

EXPERIMENTAL

Reagents. Cupric formate pure, 27—28% Cu (Koch-Light Laboratories Ltd., England), palladium(II) chloride as 40% aqueous solution (Kovohutě, Vestec), formaldehyde 36—38% aqueous solution *p.a.*, hydrochloric acid 35—38% *p.a.*, potassium hydroxide *p.a.* (all Lachema, Brno). Carriers: charcoal Supersorbon Degussa HB-3 (FRG) grain size below 0·063 mm and Dicalite C-190-N/FF (Italy) grain size average 0·002 mm. Electrolytical hydrogen (ČSN 654 435, Technoplyn, Kyje).

Preparation of catalysts. Palladium black (PB) was prepared according to ref.[4]. The other catalysts were prepared by saturation of carrier powder with palladium(II) chloride and subsequent reduction. The reduction was carried out with formaldehyde[5] (the catalysts denoted as KF, Dicalite charcoal carrier) or with hydrogen[2] (the catalysts denoted as KH, Degussa charcoal carrier) at 150°C in an apparatus[6] with mobile catalyst layer. Complete reduction with hydrogen was indicated by the absence of hydrogen chloride in the gases leaving the reactor. The same apparatus was used for activation of the catalysts KF and PB (hydrogen treatment at 150°C for 1·5 h) to give the catalysts KA and PBA, respectively. Each series involved catalysts with 1, 3, 5 and 10% (by wt.) palladium on the carrier, the percentage of active component being given in the abbreviations. Furthermore, a commercial catalyst Cherox 41—00 (CHZ ČSSP, Záluží v Krušných horách) was used under the abbreviation KP (3—4% Pd on charcoal Supersorbon Degussa).

Apparatus and procedures. The catalytic decomposition of aqueous cupric formate was carried out in a glass isothermal reactor with magnetic stirrer, using 50 ml aqueous solution of the given concentration and 0·3 g catalyst powder. In the course of the reaction 2 ml samples were withdrawn, catalyst was removed by centrifugation, whereupon colourimetric analysis was carried out and the samples were returned back in the reactor[2]. It was possible to introduce gas (hydrogen, oxygen, ethylene) into the reactor under surface of the liquid during the reaction. If not otherwise stated, the measurements were carried out at 20°C.

RESULTS AND DISCUSSION

Sorption of Cupric Formate on Charcoal

For correct interpretation of cupric formate concentration decrease due to action of the palladium catalysts in solutions it is necesssary to know the effect of the carrier itself. Fig. 1 gives the dependence of molar concentration M [mol.l^{-1}] on time t [h] for the both used charcoals (20°C, 50 ml 10% cupric formate, 0·3 g charcoal). The sorbed amount did not depend on the grain size but on the carrier type. Evacuation of the whole system and removal of air from the pores also had no influence. The

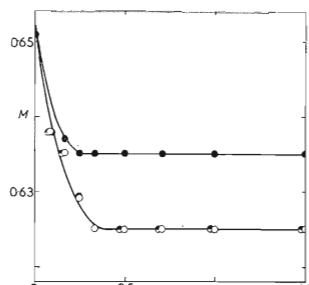

FIG. 1

Sorption of Cupric Formate on Charcoal
○ Supersorbon Degussa, 3—4 mm grain,
◓ Supersorbon Degussa, powder 0·063 mm,
● Dicalite C-190-N(FF) Nuchar, powder 0·002 mm. [M(mol . l.$^{-1}$) t(h)].

sorbed amount decreased with increasing temperature (Table I). It was found that the cupric formate concentration decrease in aqueous solution is due to both the proper sorption on the charcoal Supersorbon Degussa and decomposition by the substances present in the charcoal and extractable with water, and, therefore, we tried to separate the two phenomena by extraction of the untreated charcoal. The extracted charcoal was used for determination of the adsorbed amount, the evaporation residue from the extract was used for determination of the decomposed formate (Table I). Sum of the cupric formate amount sorbed on the extracted charcoal and that decomposed by the water-soluble extract (all measurements at 20°C) showed acceptable agreement with the cupric formate amount sorbed/decomposed by the untreated charcoal. At 90°C the above sum was by 40% higher than the value found in measurements with untreated charcoal. The determined difference is greater than a possible experimental error and indicates that co-operation of the water-extractable substances with charcoal (unpretreated charcoal) brings about a smaller cupric formate concentration decrease than that which can be ascribed to physical adsorption on the extracted carrier and decomposition caused by the extract. The substances present in the extract were liquidated during the decomposition, increased temperature also had unfavourable effect on their operation. In all the cases the cupric formate concentration in solution was fixed within 15 to 30 min. For explanation of the observed phenomena it will be necessary to identify the substances, in the present communication the effect of carrier (unpretreated charcoal) is considered as a whole.

TABLE I

Amount of Cupric Formate Sorbed/Decomposed on Charcoal Supersorbon Degussa g$(HCOO)_2Cu$/g charcoal.

Temperature °C	Adsorbed or decomposed amount		
	unpretreated charcoal	extracted charcoal[a]	extract[b]
20	0·663	0·408	0·330
50	0·408	0·280	—
90	0·332	0·230	0·236

[a] 0·3 g Unpretreated charcoal was heated with 100 ml water at 100°C 1 h. Then the charcoal was separated and dried; [b] evaporation of the water used for extraction gave 0·028 g residue which was used for decomposition of cupric formate. The given values are related to the extract amount obtained from 1 g charcoal.

Decomposition of Cupric Formate by Palladium Catalysts

Kinetics of the decomposition of cupric formate by palladium catalysts is rather complex. Fig. 2 gives the cupric formate concentration decrease in solutions (50 ml) of various concentrations caused by 0·3 g KP catalyst at 20°C. From the Fig. it is obvious that the decomposition rate increases with increasing formate concentration. The reaction rates were approximately 1. order in initial cupric formate concentration. The reaction rate decreases with time due not only to decreasing cupric formate concentration but also to gradual deactivation of the catalyst caused by the deposited copper. This fact follows from comparison of the decomposition rate of 10% solution by fresh catalyst (2) with that of the originally 20% solution after 10 h when the decomposition reaction decreased the cupric formate concentration to just 10% (1). All further measurements were carried out with the 10% solution which is stable enough to temperature changes and whose reaction rate is sufficiently high.

The above-mentioned results indicate that, in the first phase, physical adsorption of cupric formate on the carrier and active catalyst centres takes place followed by its decomposition by the substances present in the charcoal. The catalysts of the series KF (and KP) prepared by reduction with formaldehyde show then a pause in the concentration curve (Fig. 3) during which obviously the sorbed formate is decomposed and the hydrogen formed in the decomposition is dissolved in palladium whereby palladium is activated[2] so that further decomposition has an autocatalytic character. The mentioned pause is not observed with the catalysts reduced (KH) or activated (KA) with hydrogen.

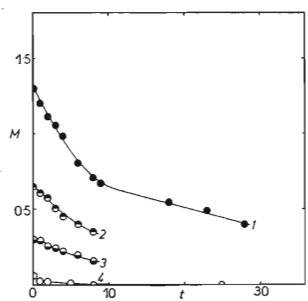

FIG. 2

Influence of Concentration of Cupric Formate Solution on Course of Decomposition
% by wt.: *1* 20; *2* 10; *3* 5; *4* 1.

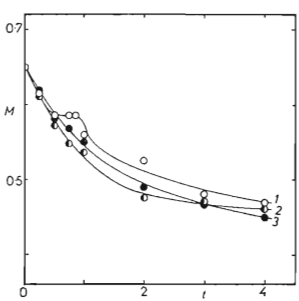

FIG. 3

Effect of Reduction Method of Catalysts on Decomposition Course
1 KF 3, *2* KH 3, *3* KA 3.

Decomposition of cupric formate by the catalyst KP was investigated at the temperatures 20, 30, 50 and 70°C. The reaction rates were obtained as differential coefficients of the concentration-time dependences at the end point of the mentioned pause. As the cupric formate concentration in these points was not the same at different temperatures (the concentration in solutions decreased with increasing temperature), the reaction rates were corrected using the presumption that the reaction rate is 1. order in cupric formate concentration. The corrected reaction rates complied very well with the Arrhenius equation, the value of apparent activation energy being 56·6 kJ/mol. Similar value (51·5 kJ/mol) was found[7] for decomposition of formic acid on palladium catalyst.

Favourable effect of hydrogen on activity of the palladium catalysts was proved also in experiments in which hydrogen was removed by introducing ethylene or oxygen into the reactor during the decomposition. Fig. 4 shows unambiguously the retarding effect of ethylene on the decomposition rate of cupric formate with the KH 10 catalyst due obviously to reaction of ethylene with hydrogen to ethane or to its competing adsorption at the catalyst surface. Substitution of ethylene by hydrogen resulted in complete recovery of the catalyst activity. Similar effects were observed in the case of oxygen.

If the catalyst was intentionally poisoned with thiophene vapours, then physical adsorption on the carrier only occurred, no decomposition of cupric formate taking place.

Table II gives the overall amount of the deposited copper calculated from the cupric formate concentration decrease through decomposition with various catalysts. After reaching the given values the catalyst was completely inactive for further decomposition. In the course of all the decompositions hydrogen was introduced into the reactor to increase the catalytic activity. The exhausted cupric formate solution

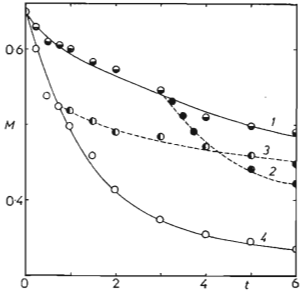

FIG. 4

Effect of Intentional Lowering of Hydrogen Concentration on Decomposition Course

4 The decomposition course in the absence of ethylene, *1* ethylene introduced into the reactor since the beginning of the decomposition, *3* ethylene introduced into the reactor for 45 min from the beginning of the decomposition, *2* 3 h after the beginning of the decomposition hydrogen introduction started instead of ethylene.

TABLE II
Total Copper Amount Deposited on Pd Catalysts (mol/mol)

Catalyst	$g_A(Cu)/g_A(Pd)$	Catalyst	$g_A(Cu)/g_A(Pd)$
KF 1	647	KH 1	659
KF 3	697	KH 3	668
KF 5	609	KH 5	623
KF 10	646	KH 10	628
PB	7·6	—	—

was replaced by fresh solution if necessary. The copper amount (mol) deposited on the individual carrier catalysts was practically (relative to the palladium content), the same, whereas the amount precipitated by the palladium black was lower by almost two orders of magnitude due to substantially lower active surface of the metal. Separate experiments showed that even the highly active copper catalyst do not cause decomposition of cupric formate. The found surprisingly high ratio $g_A(Cu) : g_A(Pd)$ is perhaps connected with the hydrogen amount which can be activated by the Pd catalyst up to its complete deactivation by the deposited copper.

This view is also supported by the results obtained with the palladium black activated by different methods. Its was found that activation of palladium black with hydrogen results not only in an increase of decomposition rate, but also conversion of cupric formate is higher on such catalyst. The highest conversion was obtained, if hydrogen was continuously introduced into the reactor during the decomposition.

Effect of Catalyst Preparation on Its Activity

The method of cupric formate decomposition in aqueous solution makes it possible to follow the effect of conditions of the catalyst preparation on its activity. It was found[2] that the catalysts reduced with hydrogen at 150°C are substantially more active than those reduced at 270°C. Influence of time of the hydrogen reduction at 150°C on activity of the palladium catalyst KH 3 is given in Fig. 5. The catalyst samples differing in reduction times were washed with water and dried before use for the cupric formate decomposition, so that the non-reduced component and hydrogen chloride (which could affect the decomposition course[2]) might be removed. The not fully reduced catalysts exhibited lower activity in the decomposition reaction. The end of the reduction was indicated by absence of hydrogen chloride in the gas leaving the reactor after reduction. After 6 h the reduction was practically finished.

Prolongation of reduction time had no effect on the catalyst activity. All the catalyst of the KH series were reduced for 8 h.

Reaction rates of the proper catalytic decomposition were read from the time dependence of molar concentration of cupric formate in the aqueous solution after elimination of physical adsorption, decomposition of formate by the substances present in the carrier, and induction period of the catalyst of KF series. In case of palladium black the initial reaction rate was read. The rates were corrected on the same cupric formate concentration by introduction of the presumption of the 1. order reaction with respect to formate concentration. Reproducibility of the kinetic measurements was very good, so that the error with which the relative activities of the individual catalysts are loaded is practically given only by inaccuracy in reading of the reaction rates as slopes of tangents at $t = 0$ (PB, KH and KA catalysts) or at the end of the induction period (KF catalysts). In the latter case the error was obviously greater, however, by assessment it did not exceed 10% of the value found. The comparison was based on the KP catalyst, relative activities for unit amounts of the catalysts are given in Table III.

The least active catalysts were those of the KF series. Their activity can be increased by activation with hydrogen, which also removes the induction period in the kinetic curves. The initial activity of palladium black was practically identical with that of the KF 5 catalyst and could be increased by activation with hydrogen. Activity decrease of palladium black during decomposition was, however, faster, which is obviously due to smaller surface and easier deactivation by the deposited copper. Activity of the carrier catalysts increased proportionally with increasing content of the active metal up to 5% by wt. on the carrier. Further increase of the active metal content had no marked effect on the catalyst activity. This trend is known from testing of activity of catalysts containing various amounts of active component

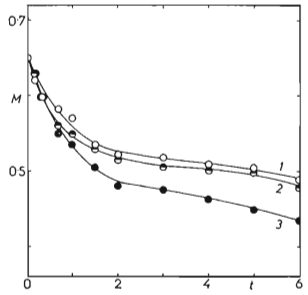

FIG. 5

Effect of Hydrogen Reduction Time on Activity of Palladium Catalysts
Reduction 1 2 h, 2 4 h, 3 6 and 8 h.

TABLE III
Relative Activities of the Used Catalysts for Decomposition of Cupric Formate

Catalyst	Relative activity	Catalyst	Relative activity
KP	1·0	KH 1	2·1
BP	4·5	KH 3	4·7
PBA	6·9	KH 5	6·8
		KH 10	5·6
KF 1	1·5	KA 1	2·0
KF 3	2·8	KA 3	3·0
KF 5	4·5	KA 5	5·7
KF 10	4·8	KA 10	5·8

in other reactions, too. In the same way low activity of palladium catalysts without hydrogen was confirmed even for such reaction which does not require hydrogen by stoichiometry.

The relative activities of the KF catalysts found in the decomposition reaction of cupric formate were compared with activities in hydrogenation of α-methylstyrene at 30°C (Table IV). The results showed good agreement (as it was the case with hydrogenation of 1-hexene[2]), which indicates the same activity trends of the individual catalysts for the both reactions. In this context it is interesting that qualitative comparison with hydrogenation of nitriles showed a reciprocal relation[9]. Obviously, active hydrogen forms acidic active centres on palladium which are active for catalytic decomposition of cupric formate. In hydrogenation of nitriles the formed

TABLE IV
Comparison of Relative Activities of KF Catalyst Series with Hydrogenation Activity

Catalyst	Relative activity	
	decomposition of $(HCO_2)_2Cu$	hydrogenation of α-methylstyrene[a]
KF 1	1·00	1·00
KF 3	1·87	2·19
KF 5	3·00	2·92
KF 10	3·20	2·92

[a] The results taken from ref.[8].

amines are bound to these centres preventing thus further hydrogenation. Acidic character of active centres of palladium on charcoal is also indicated by other facts as *e.g.* formation of hydroxyethers in reaction of oxirane compounds with alcohols in the presence of Pd/charcoal catalyst and hydrogen under mild conditions[10] or high isomerization ability of this system in hydrogenations of olefins, unsaturated alcohols and oxiranes[11]. It was confirmed that measurement of decomposition rate of cupric formate represents a suitable testing method for determination of activity of palladium catalysts.

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