STUDY OF PROPERTIES OF COPPER-MODIFIED PLATINUM CATALYSTS

Libor ČERVENÝ[a], Ivo PASEKA[b], Vladimír STUCHLÝ[a] and Vlastimil RŮŽIČKA[a]

[a] *Department of Organic Technology,*
Prague Institute of Chemical Technology, 166 28 Prague 6 and
[b] *Institute of Inorganic Chemistry,*
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received September 18th, 1980

The properties of catalysts based on platinum black modified with copper were studied. The free platinum surface area and the amount of the surface copper were determined by potentiodynamic measurements; the isosteric heats of hydrogen adsorption were also measured. The catalysts were tested in gas phase dehydrogenation of cyclohexanol; after the reaction, and also after mere thermal exposition of the catalyst to hydrogen stream, the surface of the catalysts was re-examined.

Modification of platinum- or palladium-based catalysts with Ib Group elements can have an essential impact on their catalytic properties[1-12]. The activity and selectivity of such catalysts are considerably affected by the distribution of the modifying element on the platinum metal surface and vary in dependence on its amount and on the nature of the reacting substances. Frequently the active metal and the modifying metal form alloys[5,7,11-13]. Since the alloy surface may significantly differ from the metal bulk as to the composition, the independent effect of the individual surface atoms of the alloy constituents should be considered when interpreting the relation between the catalyst composition and its catalytic effect. Information on the state of the surface thus acquires importance as it can differ considerably from the state of the unused catalyst.

In the present work, catalysts based on platinum black modified with copper were studied. The effect of the amount of copper on the activity and selectivity of the catalyst was investigated in dehydrogenation of cyclohexanol; the catalyst surface was examined before and after the reaction.

EXPERIMENTAL

Platinum black was prepared in the common fashion from H_2PtCl_6 solution by reduction with formaldehyde. Copper was applied to the platinum catalyst by adding a volume of aqueous solution fo copper formate, copper concentration $1{\cdot}9 \,.\, 10^{-3}$ g ml^{-1}, to a suspension of 7 g of platinum black in 50 ml of water; copper was deposited on the platinum within 3 h stirring. Catalysts with various copper contents were separated, washed with water, and dried to constant weight at 60°C.

The active surface area of the platinum black was determined electrochemically, by using the potentiodynamic method[13,14]. The catalyst for the measurement was pressed on a gold sheet.

The electrode was polarized by triangular voltage in the region 0·05 to 1·2 V, with the potential sweep rate 1·3 mV s^{-1}. The recorded current response was integrated to obtain the charge, from which the degree of occupation of the platinum surface by copper was calculated assuming that the charge for hydrogen oxidation was 2·08 . 10^{-4} C cm^{-2}, that for copper oxidation 4·16 . 10^{-4} C cm^{-2}. The measurements were conducted in sulfuric acid solution (2 mol dm^{-3}).

The heats of hydrogen adsorption were also determined electrochemically. The measuring electrode was prepared as in the preceding case, the measurements were conducted in sulfuric acid solution (1 mol dm^{-3}) at 70, 30, and 10°C. Increasing voltage was supplied by generator until all the hydrogen was oxidized on the catalyst surface. The amounts of the adsorbed hydrogen for the temperatures chosen and the amounts of the adsorbed hydrogen for preselected potential values were determined based on the current responses; their ratios gave then the degrees of the coverage of the free platinum surface by hydrogen for the potentials in question. The changes in the potential of hydrogen oxidation with temperature for a given degree of the coverage are given by the corresponding changes in the partial pressure of hydrogen, proportional to the isosteric heats of adsorption.

The catalytic dehydrogenation was performed in an integral glass flow-through fixed bed reactor (7 × 300 mm) accomodated in a heating jack with controlled temperature (±1°C). The catalyst (0·2 g) was activated with hydrogen at 260°C for 30 min prior to the reaction. Cyclohexanol was delivered by means of a linear doser using the rate of 0·11 mg s^{-1}. The products were collected in a freezing trap and analyzed gas chromatographically.

Analytical methods. The analyses were carried out on a Chrom 2 apparatus with flame ionization detection at 120°C. Two columns were used, length 2·5 m, inner diameter 3 mm, one

TABLE I

Parameters of the catalysts used

Catalyst No	Amount of surface copper mg Cu/g Pt		Degree of the coverage of the platinum surface by copper Θ_{Cu}	Specific surface area of platinum $m^2 g^{-1}$
	prepared	determined		
1	0	0	0·00	11·9
2	5	5·7	0·18	9·8
3	10	10·3	0·32	8·1
4	15	15·6	0·48	6·2
5	20	19·2	0·59	4·9
6	25	23·2	0·70	3·6
7	30	23·9	0·75	3·0
8	35	27·9	0·80	2·4
9	40	28·2	0·86	1·7
10	45	28·7	0·89	1·3
11	50	29·3	0·90	1·2

packed with 15% SE 31 silicone elastomer, the other with 15% Carbowax 20 M, always on Chromaton NAW-HMDS. On the first column, the amounts of the cyclohexane–benzene mixture, cyclohexanol–cyclohexanone mixture, and phenol were determined. On the second column, the amounts of cyclohexane, benzene, cyclohexanol, and cyclohexanone were analyzed; phenol did not elute.

RESULTS AND DISCUSSION

The characteristics of eleven prepared catalysts, as obtained from the potentiodynamic measurements, are given in Table I. As is apparent from a comparison of the two first columns, the amount of the determined surface copper at its higher contents is lower than as would correspond to the preparation procedure. We are so far unable to offer a unique explanation of this fact; possibly, copper penetrates into the platinum phase even at ambient temperature, similarly as is the case with Pd–Cu systems[11,15].

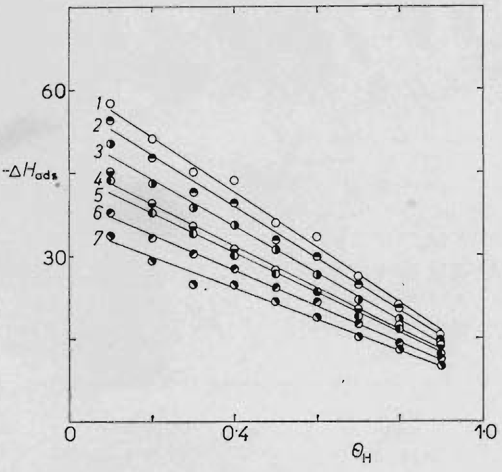

FIG. 1

Dependence of the isosteric heat of adsorption of hydrogen on the degree of the coverage of free platinum surface by hydrogen Θ_H for the various catalysts. Θ_{Cu}: *1* 0·00, 2 0·18, *3* 0·32, *4* 0·48, *5* 0·59, *6* 0·70, 7 0·75

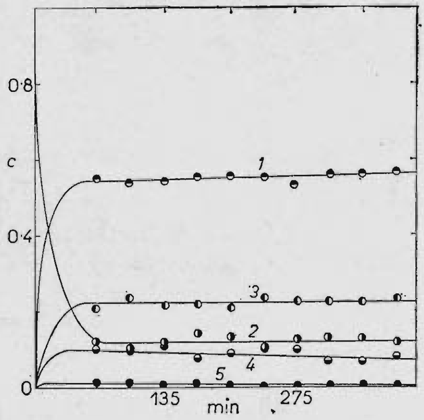

FIG. 2

Time course of composition of the reaction mixture from dehydrogenation of cyclohexanol. $(\Theta_{Cu})_{initial} = 0·75$; *1* phenol, *2* cyclohexanol, *3* cyclohexanone, *4* benzene, *5* cyclohexane; *c* is dimensionless concentration represented by the ratio of the instantaneous concentration of the substance to the initial concentration of cyclohexanol

The isosteric adsorption heats of hydrogen[16,17] as determined potentiodynamically are given in Fig. 1. The values decrease with increasing degree of coating of the platinum surface by hydrogen (Θ_H), which points to a considerable heterogeneity of the surface; obviously, the unoccupied surface is more homogeneous than the initial surface.

The values of the adsorption heats for zero degree of coating of the surface by hydrogen ($-\Delta H_{ads}$) were obtained from the measured data by extrapolation;

TABLE II

Heats of adsorption of hydrogen for zero degree of the coverage of the catalyst surface by hydrogen

Degree of the coverage of the platinum surface by copper Θ_{Cu}	k^a	$-\Delta H_{ads}$ kJ mol^{-1}
0·00	0·826	61·0
0·18	0·807	57·0
0·32	0·802	52·4
0·48	0·791	45·7
0·59	0·790	45·6
0·70	0·783	40·0
0·75	0·776	35·0

[a] Constant in Eq. (*1*).

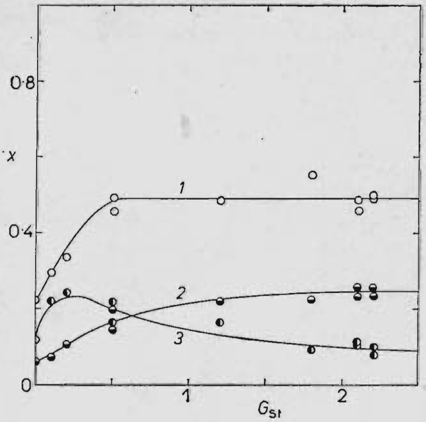

FIG. 3

Dependence of the degree of conversion of cyclohexanol to the products x on the amount of surface copper determined after the dehydrogenation (mg Cu/g Pt). *1* Phenol, *2* cyclohexanone, *3* cyclohexane and benzene they are given in Table II along with the values of the constant k characterizing the heterogeneity of the catalyst surface in the semi-empirical relation

$$H_{\mathrm{ads}} = H^{0}_{\mathrm{ads}}(1 - k\Theta_{\mathrm{H}}) . \qquad (1)$$

At elevated temperatures, Pt–Cu alloy can be expected to form in the surface layers, which in fact leads to a new catalyst; therefore, after washing the catalyst with hydrogen for at least 30 min after the completed dehydrogenation to remove adsorbed organics from the surface, the platinum surface area and the amount of the surface copper were subsequently determined potentiodynamically. These parameters were also determined for catalysts only exposed to the action of hydrogen at the same temperature. The values measured are given in Table III.

As follows from a comparison with Table I, thermal exposition in hydrogen atmosphere as well as exposition prior to the dehydrogenation process results in a considerable reduction in the specific surface area of platinum, obviously due to sintering of its crystallites. At the same time the charge for oxidation of copper in the potentiodynamic determination diminished appreciably, so that copper practically could not be determined. This bears out the concept of formation of Pt–Cu alloy, although a direct proof by X-ray diffraction analysis could not be obtained because of the

TABLE III

Effect of the use in dehydrogenation and of thermal exposition on the surface of the catalysts

Catalyst No	Amount of surface copper mg/g Pt		Specific surface area of platinum $m^2 g^{-1}$	
	after dehydrogenation	after thermal exposition	after dehydrogenation	after thermal exposition
1	0	0	4·7	4·8
2	0·1	—	4·2	—
3	0·2	0·2	4·3	1·9
4	0·5	—	4·0	—
5	0·5	—	3·9	—
6	1·2	—	3·5	—
7	1·8	2·2	2·7	1·6
8	2·1	—	2·1	—
9	2·2	—	1·5	—
10	2·1	—	1·5	—
11	2·2	2·5	1·4	1·5

very low copper content in the catalyst. The differences in the amount of the surface-bonded copper and the specific surface area of platinum for thermally exposed catalysts and for catalysts used in dehydrogenation obviously stem from the fact that the sintering processes are affected by the nature of the substances with which the catalyst surface is in contact. The concept of the Pt–Cu alloy formation is also supported by the potentiodynamic measurements with catalysts with higher copper contents. A catalyst with the degree of the coverage of the platinum surface by copper equal to unity was found[12] to contain more than 1 $m^2 g^{-1}$ unoccupied platinum surface after 30 min exposition in hydrogen stream at 260°C, so that in fact, uncovering of the free surface took place in this case.

In the dehydrogenation of cyclohexanol, we may suume that phenol is formed on the platinum active centres only, whereas cyclohexanone is formed both on platinum and on copper. In addition to these substances, benzene and cyclohexane were also identified in the reaction mixtures, which can be explained, *e.g.*, in terms of hydrogenolytic reactions. The time course of the composition of the reaction mixture from dehydrogenation of cyclohexanol (Fig. 2) shows that the steady state establishes rather rapidly.

The dependence of the degree of conversion of cyclohexanol on the amount of the surface copper (determined after the dehydrogenation, Table III) is depicted in Fig. 3. The activity and selectivity of the catalyst varied appreciably up to the surface copper content of approximately 1·3 mg Cu/g Pt (hence 25 mg Cu/g Pt for the unexposed catalyst), at higher contents they remained roughly constant. The fact that in the region of low copper contents in the catalyst the activity increased with the copper content is to be ascribed to the higher activity of the platinum–copper alloy in the process as compared with pure platinum. If benzene and cyclohexane are looked upon as undesirable products, it is advisable from the points of view of both selectiivty and activity to employ catalysts whose contents of surface copper are 1·2 mg Cu/g Pt or more.

REFERENCES

1. Sokolskii D. V., Zakumbaeva G. D.: *Adsorbtsiya i Kataliz na Metallakh VIII. Gruppy v Rastvorakh.* Izd. Nauka Kaz. SSSR, Alma Ata 1973.
2. Rienäcker G., Vornum G.: Z. Anorg. Allg. Chem. *283*, 287 (1956).
3. Rienäcker G., Sarry B.: Z. Anorg. Allg. Chem. *257*, 41 (1948).
4. Rienäcker G., Müller E., Burmann R.: Z. Anorg. Allg. Chem. *158*, 95 (1943).
5. Davies E. E., Elkins J. S., Pickethly R.: Ger. Offen. 2 117 651 (1973).
6. Bizhanova N. B., Erzhanova M. S., Sokolskii D. V.: Izv. Akad. Nauk Kaz. SSR *19*, 15 (1969).
7. Mallát T., Petró J., Polyanzsky E., Mathé T.: Acta Chim. (Budapest) *90*, 333 (1976).
8. Mokrousov P. V., Naumov A. I.: U.S.S.R. 168 302 (1965).
9. De Thomas W. R., Hort E. V.: Ger. Offen. 2 602 894 (1976).
10. Elkins J. S.: Brit. 1 328 532 (1973).

11. Mallát T., Petró J., Schaffer M.: Acta Chim. (Budapest) *98*, 175 (1967).
12. Mach J.: *Thesis*. Prague Institute of Chemical Technology, Prague 1979.
13. Kinoshita K., Stonehart P.: Modern Aspects of Electrochemistry *12*, 225 (1977).
14. Paseka I., Červený L., Mach J., Růžička V.: This Journal *45*, 3541 (1980).
15. Szabó S., Nagy F.: J. Electroanal. Chem. Interfacial Electrochem. *70*, 357 (1976).
16. Frumkin A. N.: Zh. Fiz. Khim. *14*, 1200 (1940).
17. Sokolskii D. V., Sokolskaya A. M.: *Metallly — Katalizatory Gidrogenizatsii.* Izd. Nauka, Akad. Kaz. SSR, Alma Ata 1970.

Translated by P. Adámek.