HYDROGENATION OF 2-PHENYL-1-PROPENE
ON PLATINUM BLACK MODIFIED WITH COPPER

Ivo PASEKA[a], Libor ČERVENÝ[b], Josef MACH[b] and Vlastimil RŮŽIČKA[b]

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

Copper deposited from a solution of copper(II) formate on Pt-black at surface coverage lower than unity is present on the platinum surface both in the form of ad-atoms and in the form of multiatomic layers. From the dependence of the hydrogenation rate on coverage by copper it followed that the reaction rate depended on the number of free pairs of the adsorption sites of platinum unoccupied by copper.

The influence on the electrochemical activity of platinum in the oxidation of some organic compounds exercised by ad-atoms of metals on the electrode surface has been reported in several papers[1,2]. In hydrogenation reactions on platinum catalysts the adsorbed ad-atoms of metals which do not adsorb hydrogen, unlike electrooxidation reactions, reduce only more or less the activity of Pt-black[3]. Foreign atoms present at the surface that are unable to adsorb hydrogen or an organic molecule, reduce the catalytically active surface of the catalyst and moreover diminish the probability of the presence of adjacent sites occupied by hydrogen and by an organic molecule; this in turn further reduces the rate of hydrogenation.

It was the aim of this study to find quantitative relationships between the degree of coverage of platinum surface by copper, on the one hand, and the rate of hydrogenation of 2-phenyl-1-propene, on the other, thus contributing to the elucidation of the mechanism of the hydrogenation process.

EXPERIMENTAL

Platinum black was prepared in the usual way from a H_2PtCl_6 solution by reduction with formaldehyde. Copper was deposited on Pt-black from a solution of copper formate[4]; the calculated amount of 0·07% solution was pipetted into a suspension of the catalyst in 50 ml distilled water. The suspension was stirred for three hours, and after that copper was deposited quantitatively on Pt-black. The Pt–Cu catalysts thus prepared were removed by filtration, washed with water and dried at 60°C.

The active surface of Pt-black was determined by the electrochemical-potentiodynamical method. About 20 mg the catalyst was pressed on Au sheet 1·8 cm in diameter which was then fixed in a Teflon holder and with it placed in an electrolytic cell with a solution of 2M-H_2SO_4. The electrode was introduced into solution with a switched-on potentiostat at the potential

($+0.05$ V against R.H.E.)., in order to prevent the dissolution of copper from the catalyst surface. After removal of the dissolved oxygen from solution by bubbling with nitrogen, the electrode was polarized with triangular voltage in the range 0.05—1.2 V with the sweep rate 1.3 m V s^{-1}. The current response corresponding to the oxidation of adsorbed hydrogen and of deposited copper was integrated. The charge thus obtained was used for calculating the free surface of platinum and that occupied by copper, assuming that the oxidation charge of adsorbed hydrogen and that of copper on 1 cm^2 were $208 . 10^{-6}$ and $416 . 10^{-6}$ C cm^{-2} respectively.

Activity. 2-Phenyl-1-propene (1 ml) was hydrogenated at 20°C and atmospheric pressure in a stirred glass reactor in toluene (10 ml) using 0.1 g of catalyst. The reaction rate was determined from the time dependence of the consumption of hydrogen.

RESULTS AND DISCUSSION

Information on the character and amount of the individual types of deposited copper (monolayer or multiatomic layer) is provided by potentiodynamic curves, namely, by the position of the oxidation peak and by the charges of hydrogen and copper represented by the area of the peak (Fig. 1). Fig. 2 demonstrates the dependence of $A = Q_{Cu}/2(Q_H^0 - Q_H)$, where Q_{Cu} is the oxidation charge of copper, Q_H^0 that of hydrogen on Pt-black without copper and Q_H that on Pt-black with copper, on the free surface of platinum. The value A is in fact the ratio of the total number of atoms of deposited copper to the number of atoms deposited in the form of a monolayer. The effect of the degree of surface coverage by copper on the rate of hydrogenation of 2-phenyl-1-propene can be seen in Fig. 3. The hydrogenation rate decreases monotonously with decreasing free surface able to adsorb hydrogen.
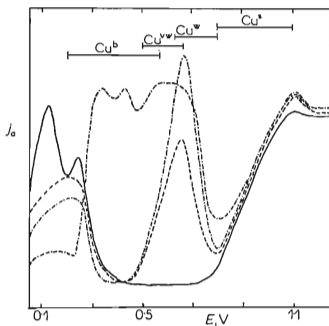

Fig. 1

Potentiodynamic Oxidation Curves of Pt and Pt–Cu Blacks

Cu content: ——— 0, – – – 0.0109, — · — 0.0126, –·–·– $0.035 g_{Cu}/g_{Pt}$. Cu^b domain of oxidation of metallic copper, Cu^{vw} very weakly, Cu^w weakly, Cu^s strongly adsorbed copper atoms[5].

The form of potentiodynamic curves has indicated (Fig. 1) that under given conditions copper is deposited only exceptionally as a monolayer and that in most cases, especially at larger coverage of copper, the latter is present on the surface both in the form of weakly and strongly adsorbed ad-atoms (oxidation potential 0·6 to 0·8 V and 0·8 − 1·1 V) and in the form of metallic copper which becomes oxidized at $E \simeq 0·2 − 0·6$ V. These qualitative conclusions have been confirmed by quantitative values of A, which almost at all degrees of surface coverage by copper are higher than unity (Fig. 2). These A values, in spite of their large scatter, indicate nevertheless that copper only rarely is deposited on the surface of Pt-black as a monolayer and a multiatomic layer is formed in most cases. This finding is in agreement with the results of Szabo and Nagy[5], who found that copper was first deposited on Pt-black in several layers, and the coating with monolayer was possible only if the second and further layers of atoms were dissolved and again deposited on the free platinum surface.

The rate of hydrogenation of 2-phenyl-1-propene both on Pt and Pt–Cu black is a zero-order reaction with respect to the concentration of 2-phenyl-1-propene in solution. It follows from the results obtained by Sokolskii and coworkers[3] that hydrogenation proceeds at $E \simeq 0·30$ V; in other words, the catalyst surface is covered predominantly by the adsorbed reactant, and the reaction product is not adsorbed on the catalyst surface. In the hydrogenation reaction, the hydrogen molecule must be
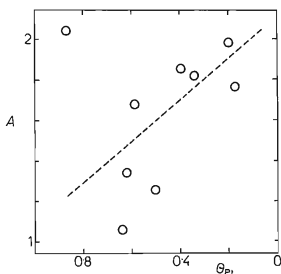

Fig. 2

The Dependence of the Ratio of the Total Number of Atoms of Deposited Copper to the Number of Atoms Deposited as Monolayer (A) on the Degree of Free Platinum Surface
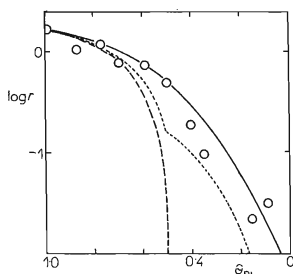

Fig. 3

The Dependence of the Rate of Hydrogenation r on the Degree of Free Platinum Surface

○ Experimental points. Theoretical curves according to Eqs (1), (2) for various S: ——— $S = 0$, — — — — $S = 0·8$, — — — $S = 1$.

in the first step dissociatively adsorbed on the unoccupied platinum surface; in further steps, the adsorbed molecule of 2-phenyl-1-propene reacts with adsorbed hydrogen. If the molecule of 2-phenyl-1-propene is adsorbed by opening the double bond on two adsorption sites, then in the first reaction step of hydrogenation an interaction should occur between three neighbouring sites occupied simultaneously by the molecule of phenylpropene and by adsorbed hydrogen. However, the dependence of the rate of hydrogenation of free platinum surface unoccupied by copper does not correspond to this step. In a paper by Furuya and Motoo[6] it has been shown that the rate of the hydrogen evolution determined by the rate of recombination of hydrogen atoms adsorbed on the nearest adjacent sites depends on the number of free pairs of platinum atoms unoccupied by copper according to the relations

$$r = kNZX_{P_t}^2(1 - S^2)/2 \quad \text{for} \quad X_{P_t} \leqq 0 \cdot 5 \qquad (1)$$

$$r = kNZ[X_{P_t} - (1 - X_{P_t})^2 S^2]/2 \quad \text{for} \quad X_{P_t} \geqq 0 \cdot 5 \,, \qquad (2)$$

where N is the overall number of surface atoms, Z is the number of the nearest neighbours, X_{P_t} is the fraction of platinum atoms and S is the degree of order of distribution of copper atoms on the surface $(S = 1$ corresponds to the highest degree of order, where the copper atoms occupy the second next adsorption sites with a strong interaction with the underlaying platinum atoms).

The experimentally determined dependence of the rate of hydrogenation on the degree of free platinum surface unoccupied by copper is close to the theoretical curve derived for the case of the disordered coverage. This suggests that the conclusive factor in the rate determining step is not simultaneous occurrence of three or more free neighbouring atoms, but only the number of adjacent pairs of platinum atoms unoccupied by copper. Such a rate determining step may either consist in the interaction of the molecule of phenylpropene, which however is adsorbed only on a single adsorption site, with the adjacent adsorbed hydrogen atom, or the dissociative adsorption of hydrogen, also requiring two free adjacent adsorption sites. The observed dependence of the rate of hydrogenation on free platinum surface does not allow us to discerne the two possible mechanisms just mentioned. In agreement with the view postulated by Sokolskii and based on the dependence of the catalyst potential in the course of hydrogenation reaction, it seems more likely that the limiting step should be the dissociative adsorption of hydrogen.

REFERENCES

1. Adzhich R. R., Simich D. N., Drazhich D. M., Despich A. Q.: J. Electroanal. Chem. Interfacial Electrochem. *61*, 117 (1975).
2. Watanabe M., Motoo S.: J. Electroanal. Chem. Interfacial Electrochem. *60*, 259 (1975).

3. Sokolskii D. V., Zakumbaeva G. D.: *Adsorpciia i Kataliz na Metallach* VIII. *Gruppy v Rastvo-rach.* Izd. Nauka Kaz. SSR, Alma Ata 1973.
4. Červený L., Marhoul A., Červinka K., Růžička V.: J. Catal. *63*, 491 (1980).
5. Szabó S., Nagy F.: J. Electroanal. Chem. Interfacial Electrochem. *70*, 357 (1976).
6. Furuya N., Motoo S.: J. Electroanal. Chem. Interfacial Electrochem. *72*, 165 (1976).
7. Sokolskii D. V., Zakumbaeva G. D., Popova N. M.: *Katalizatory Gidrogenizacii.* Izd. Nauka Kaz. SSR, Alma Ata 1975.