

## HYDROGENATION OF AROMATIC NITRO COMPOUNDS ON COPPER-MODIFIED PLATINUM CATALYSTS

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The gas and liquid phase hydrogenations of nitrobenzene and liquid phase hydrogenation of *p*-chloronitrobenzene on Pt—Cu catalysts were studied. The effect of the copper content on a catalyst was examined, and a relationship was sought between the degree of occupation of the platinum surface by copper and the decrease in the hydrogenation activity in the liquid phase hydrogenation of nitrobenzene. The mechanism of this reaction is discussed.

The properties of platinum and palladium catalysts can be modified by introducing several metals, of which copper is frequently used<sup>1-11</sup>. Copper atoms usually cause a decrease in the hydrogenation activity of platinum<sup>1</sup>. They induce changes in the size distribution and mutual distance of the platinum active centres, whereby the selectivity of the reaction may be affected. The mobility of the metal atoms increases with increasing temperature, bringing about agglomeration of the platinum or palladium crystallites. Copper present on the catalyst surface diffuses into the metal bulk at higher temperatures, forming alloys with the metals<sup>7-11</sup>. Copper-modified platinum and palladium catalysts have been applied, among other things, to hydrogenation of aromatic nitro compounds<sup>2-4</sup>; in these works, the activity of the catalysts has been tested and the selectivity measured in hydrogenation of chlorinated nitrobenzenes.

In the present work, gas and liquid phase hydrogenations of nitrobenzene on Pt—Cu catalysts have been studied with the aim to gain new information on the mechanism of this reaction. In the hydrogenation of *p*-chloronitrobenzene, the possibility has been investigated of suppressing the hydrogenolysis of chlorine by employing copper-modified platinum catalysts.

### EXPERIMENTAL

*Catalysts.* Copper was deposited on platinum black by decomposing copper(II) formate in aqueous solution<sup>5,6</sup> in quantities of 0–50 mg Cu/g Pt. In this manner, a series of eleven catalysts was prepared with different contents of copper. The free platinum surface and the surface copper on the catalysts were determined by the electrochemical potentiodynamic method<sup>6,11</sup>.

*Gas phase catalytic hydrogenation of nitrobenzene* was conducted in an integral flow-through fixed bed reactor ( $7 \times 200$  mm) placed in a heating jacket with controlled temperature ( $130 \pm \pm 1^\circ\text{C}$ ). The catalyst (0.1 g) was activated in hydrogen stream at  $130^\circ\text{C}$  for 30 min prior to the reaction, nitrobenzene and hydrogen were then fed into the reactor in the ratio 1 : 200, with the nitrobenzene flow rate  $0.11 \text{ mg s}^{-1}$ . The products leaving the reactor were frozen out and gas chromatographically analysed.

*Liquid phase hydrogenations of nitrobenzene and p-chloronitrobenzene* were carried out on a routine apparatus<sup>12</sup> at  $20^\circ\text{C}$  and normal pressure. 10 ml of solution of nitrobenzene (0.12 g) or *p*-chloronitrobenzene (0.15 g) in ethanol and 0.005–0.1 g amount of the catalyst were used (the weight of the catalyst was increased proportionally to the degree of coating the surface by copper). The course of the hydrogenation was monitored by measuring the time dependence of the hydrogen takeup and by simultaneous chromatographic analysis of the samples.

*Analytical methods.* The analyses were performed on a Chrom-2 gas chromatograph with flame ionization detection. The products of hydrogenation of nitrobenzene were analyzed on column 2.5 m long packed with 15% Apiezon L on Chromaton NAW-HMDS at  $160^\circ\text{C}$ , the products of hydrogenation of *p*-chloronitrobenzene, on a similar column packed with 15% silicone elastomer SE 31 on Chromaton NAW-HMDS at  $140^\circ\text{C}$ .

## RESULTS AND DISCUSSION

In the hydrogenation of nitrobenzene on Pt—Cu catalysts, it can be assumed that the hydrogenation of the aromatic ring can be catalyzed only by platinum, whereas the reduction of the nitro group can occur both on platinum and, at higher temperatures, also on copper.

In the gas phase hydrogenation of nitrobenzene at  $130^\circ\text{C}$ , the conversion of nitrobenzene in the arrangement used was complete in all cases. The results shown in Fig. 1 thus may in part be affected by the possible consecutive reactions; the trends established, however, are obviously of general validity. Fig. 1 shows the effect of the copper content in the catalyst (for equal catalyst amounts) on the composition of the reaction products of the nitrobenzene hydrogenation. Although the effect of the copper content in the catalysts on their total activity could not be specified, the selectivity of hydrogenation of nitrobenzene to aniline was found to be significantly affected, increasing with the copper content up to 100% for the sample containing 50 mg Cu/g Pt. At the same time, the amount of benzene in the reaction product decreased.

In the case of the liquid phase hydrogenation in normal conditions, only the platinum-catalyzed reduction of nitro groups to amino groups occurred. The reaction rate was zero order with respect to nitrobenzene, and decreased virtually linearly with the degree of coating the platinum surface by copper, as can be seen from Fig. 2.

Copper on the platinum surface reduces the catalytically active surface area and, first of all, lowers the probability of a simultaneous occurrence of the sorbed hydrogen and the organic molecule in a mutual neighbourhood. Under the assumption that interaction of two neighbouring centres occupied by hydrogen and nitrobenzene

is necessary in the rate determining step of the reaction, the specific reaction rate (reaction rate per unit free platinum surface area) should decrease with increasing degree of occupation of the platinum surface by copper<sup>13</sup>. However, Fig. 2 demonstrates that in the case under study, the specific reaction rate is independent of the degree of coating.

For a reaction governed by recombination of two atoms sorbed on mutually neighbouring sites (which is the case with the electrochemical evolution of hydrogen), Furuya and Motoo<sup>13</sup> have suggested a relation represented graphically by the curves  $S = 1$  and  $S = 0$  in Fig. 3, where  $S$  denotes the degree of ordering in the distribution of copper atoms on the surface ( $S = 1$  corresponds to the maximum order, where the copper atoms occupy the second nearest adsorption sites with a strong interaction with the substrate Pt atoms). The experimental points lie above the theoretical curves across the entire region.

As is apparent from Fig. 3, the hydrogenation rate is higher than as corresponds to the assumption of a mutual interaction of two active centres during the dissociative adsorption of hydrogen, for which the curves  $S = 0$  and  $S = 1$  have been calculated. This indicates that in the rate determining step the occurrence of two or more neigh-

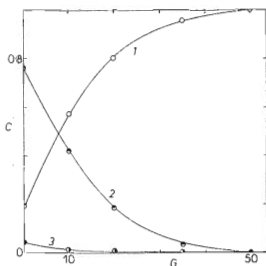


FIG. 1

Effect of the copper content in the catalyst on the composition of products of gas phase hydrogenation of nitrobenzene;  $C$  is the dimensionless concentration (instantaneous concentration of the substance with respect to the initial concentration of nitrobenzene),  $G$  is the content of copper in the catalyst (mg Cu/g Pt). 1 aniline, 2 cyclohexylamine, 3 benzene

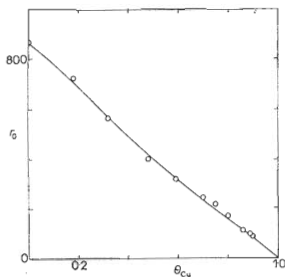


FIG. 2

Dependence of the nitrobenzene hydrogenation rate on the degree of coating of the platinum surface by copper ( $\theta_{Cu}$ ).  $r_0$  is the hydrogenation rate (ml  $H_2$ /min  $g_{cat}$ )

bouring free platinum atoms is not necessary, hence, that the hydrogenation rate is controlled neither by the interaction of the adsorbed nitro compound with hydrogen nor by the rate of the dissociative adsorption of the latter. The experimental results support the concept proposed by Sokolskii<sup>14</sup>, according to which the reduction of the nitro group proceeds *via* a stage of formation of the  $C_6H_5NO_2^{(-)}$  anion-radical, which in turn reacts with hydrogen in any form present in the reaction mixture, and the rate-determining factor is the electron transfer from the catalyst to the nitrobenzene molecule.

In the case of the hydrogenation of chlorinated aromatic nitro compounds on platinum metals, chlorine is also often split off in addition to the reduction of the nitro group<sup>15-17</sup>. The dechlorination on platinum is slower than on other platinum metals<sup>15</sup>, and modification of the catalysts by copper brings about suppression of the detachment of chlorine<sup>3,4</sup>. The main hydrogenation product is chloroaniline, a lesser amount of aniline is formed obviously through its hydrogenolysis or through hydrogenolysis of the starting chloronitrobenzene<sup>17</sup>. The hydrogenation rate on all the catalysts was zero order with respect to *p*-chloronitrobenzene and decreased linearly with increasing degree of occupation of the platinum surface by copper. In the same sense, but considerably more rapidly, the rate of hydrogenolysis decreased as well.

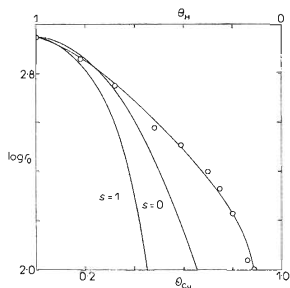


FIG. 3

Dependence of the logarithm of the nitrobenzene hydrogenation rate on the degree of coating the platinum surface by copper ( $\theta_{Cu}$ ).  $r_0$  is the initial hydrogenation rate (ml  $H_2$ /min  $g_{cat}$ ),  $\theta_H$  is the degree of coating the platinum surface by hydrogen in the absence of nitrobenzene

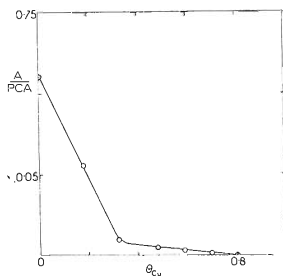


FIG. 4

Effect of the degree of coating the platinum surface by copper ( $\theta_{Cu}$ ) on the selectivity of hydrogenation of *p*-chloronitrobenzene.  $A/PCHA$  is the concentration ratio of aniline to *p*-chloroaniline at the moment of total conversion of *p*-chloronitrobenzene

Fig. 4 demonstrates that the amount of aniline in the reaction mixture (at the moment of attaining the complete conversion of chloronitrobenzene) drops rapidly with increasing degree of coating the platinum surface by copper; in the case of the catalyst with  $\vartheta_{\text{Cu}} = 0.8$  the formation of *p*-chloroaniline is selective.

In this manner it has been confirmed that modification of platinum catalysts by copper affects considerably their properties in the hydrogenation of aromatic nitro compounds. The selectivity of both the gas phase hydrogenation of nitrobenzene to aniline and the liquid phase hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline increased with increasing content of copper on the catalyst surface. The results of the liquid phase hydrogenation of nitrobenzene indicate that the rate-determining step does not require the presence of two or more active platinum centres in mutual neighbourhood.

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