BEHAVIOR OF SKELETAL COPPER-PALLADIUM CATALYSTS IN ENANTIO-

SELECTIVE HYDROGENATION

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In connection with a study of the mutual influence of the components in bimetallic dissymmetric catalysts on their capability for enantioselective hydrogenation, which has been discussed in the example of the Ru-Cu system [1], we have investigated the Pd-Cu system and its behavior in this reaction.

#### EXPERIMENTAL

Skeletal copper palladium catalysts (SCPC) were prepared by leaching the Al from finely crushed Pd-Cu-Al alloys with a 10% NaOH solution at 50°C. The alloys contained 70% Al by weight and various quantities of Pd and Cu. The contents of Pd and Cu in the original alloys and in the SCPCs were determined by chemical analysis. The alloys and the catalysts were investigated by means of x-ray phase analysis in a DRON-2 unit ( $CuK_{\alpha}$  radiation). The compositions of the phases were evaluated on the basis of the Vegard rule. The adsorption of  $H_2$ on the catalysts was studied by obtaining charging curves (CC) and potentiodynamic  $I-\varphi$  curves in 0.1 N  $H_2SO_4$  solution with a P-5827 potentiostat [2]. The catalysts were modified with a 0.5% solution of R,R-(+)-tartaric acid (100 ml, 50°C, 1 h). The hydrogenation of ethyl acetoacetate (EAA) was performed in ethanol solution in an autoclave (100°C, 100 atm). The EAA before hydrogenation was dried over MgSO4 and vacuum-distilled. The hydrogenated products were analyzed by GLC in a Khrom-31 instrument; the dispersion of optical rotation of the catalysate was measured in a Spektropol-1 instrument. The reaction rate was calculated from the formula  $v = \alpha \cdot y/m \cdot t$ , where  $\alpha$  is the initial mass of EAA (mmoles); t is the time (min) to reach a given degree of EAA conversion (%); m is the mass of catalyst (g); v is the reaction rate.

# DISCUSSION OF RESULTS

A comparison of the results obtained by x-ray phase analysis of the original alloys and the catalysts showed that the catalysts, after leaching, did not contain any Al phase. On the diffractograms of the SCPCs, lines pertaining to Pd, Cu, and  $Al_2O_3 \cdot 3H_2O$  (bayerite) were present. On the basis of the values of the lattice constants of the metals, it was concluded that, depending on the composition, the metallic phases existing in the SCPCs are Pd and Cu or a solid solution based on Pd (Table 1).

Electrochemical studies of the Pd-Cu system encountered considerable difficulty because of the ready oxidizability of the copper. In this connection, in order to ensure similarity of the processes of  $H_2$  adsorption and desorption, the polarization currents were lowered as the content of Cu in the catalyst was increased. For the samples with Pd contents below 5% (at.), the charging curves (CC) could not be taken at all. For the other catalysts, the curves that were obtained had very little hysteresis between the cathodic and anodic branches, so that we can consider the state of the system as sufficiently close to equilibrium.

From the shape of the CC taken from the skeletal Pd, we can conclude (Fig. 1) that the sorption of H<sub>2</sub> proceeds with the formation of the  $\alpha$ -phase in the interval of potentials 0.050-0.290 V. The potential we obtained for the  $\alpha$ - $\beta$  phase transition - 0.05 V - and the shape of the curve are analogous to what was observed in [2, 3]. The H/Pd ratio in the  $\alpha$ -phase was found to be 0.1. For the CCs of the SCPCs (see Fig. 1), in comparison with the CC of the Pd, there was a less sharp transition from the hydrogen region to the bilayer

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TABLE 1. Phase Composition, Adsorption Capability, and Catalytic Activity of SCPCs

Content of Cu + Pd in catalyst, wt.go	Content of Pd in metallic phase, at.%	Phases	Content of Pd in alloy phase, at.%	Surface area of Pd, m <sup>2</sup>		ratio Cu)	of complete 1 of H, V	EAA hydrog- enation rate, mmoles/min	
				per gram of catalyst	per gram of Pd	Atomic H/(Pd +	Potential desorption	per m <sup>2</sup> of cata - lyst	per m <sup>2</sup> of Pd
49,0 51,2 53,9 42,1 45,0	5,1 15,1 34,0 56,5 100	Cu; Cu-Pd; $Al_2O_3 \cdot 3H_2O$ Cu; Pd; $Al_2O_3 \cdot 3H_2O$ Cu; Pd; $Al_2O_3 \cdot 3H_2O$ Cu; Cu-Pd; $Al_2O_3 \cdot 3H_2O$ Cu; Cu-Pd; $Al_2O_3 \cdot 3H_2O$ Pd; $Al_2O_3 \cdot 3H_2O$	87,5 - 78,0	0,05 0,35 12,2 22,5 28,2	1,3 3,5 40 77 48	0,0001 0,0011 0,031 0,060 0,1	0,034 0,045 0,065 0,074 0,290	24,1 27,5 34,2 51,8 85,0	480 78 2,8 2,3 3,0

region, earlier oxidation of the surface, and absence of the horizontal section corresponding to the  $\alpha$ - $\beta$  transition. Also, in the case of the SCPCs, the hydrogen region of the CCs is much diminished, indicating a decrease in the quantity of sorbed H<sub>2</sub> when the change is made from the Pd to the SCPC. From a comparison of the potentials corresponding to the hydrogen region, it follows that the introduction of the Cu into the Pd leads to a decrease of the strength of bonding of the H<sub>2</sub> to the catalyst (see Table 1). The observed differences in adsorption capability of the SCPCs from that of the Pd itself increases with increasing content of Cu in the catalyst.

The I- $\phi$  curves of the SCPCs were taken in the potential interval 0.050-0.250 V. With a potential sweep rate of 1/3 mV/sec, the anodic and cathodic branches of the I- $\phi$  curves are close to each other, indicating reversibility of the H<sub>2</sub> adsorption processes taking place under these conditions. The I- $\phi$  curves of the SCPCs have a single current maximum, indicating adsorption of the H<sub>2</sub> on the catalysts in only one energy form. A comparison of the shapes of the anodic and cathodic curves indicates quite good reversibility of the process.

From the CCs that were obtained, we calculated the quantity of H<sub>2</sub> adsorbed on the catalysts. The start of adsorption was determined on the basis of the transition of the rather flat section of the CC to a sharply rising section of the curve, applying a correction for the capacitance of the electric double layer. From the values obtained for the quantity of adsorbed H<sub>2</sub>, we calculated the specific surface area of the Pd in the catalysts, since the Cu does not adsorb hydrogen. Here it was assumed that  $213 \cdot 10^{-6}$  C is required to remove H atoms from 1 cm<sup>2</sup> of Pd surface. These quantities were also calculated from the I- $\phi$  curves of the SCPCs. The calculations showed that the two electrochemical methods give comparable results.

From the dependence of the atomic ratio H/(Pd + Cu) on the SCPC composition (Fig. 2), it can be seen that the points corresponding to the catalysts with comparatively large contents of Pd fall on the additive line, indicating that the fraction of Pd on the surface is very close to that in the bulk catalyst. For the SCPCs with small contents of Pd, the fraction of Pd on the surface proves to be considerably smaller than that in the bulk catalyst. Apparently the small volumes of Pd or Cu-Pd alloy are covered over by the considerably greater volumes of the Cu phase.

Summarizing, we should note that in this series of catalysts we have investigated, regardless of whether the Pd forms a separate phase or dissolves Cu, the adsorption properties of the palladium are very much changed by the presence of the copper; i.e., we can say that the Cu eliminates the characteristic features of Pd with respect to  $H_2$  adsorption and brings its properties in the mixed catalysts close to the properties of Ru in analogous systems [1, 4].

The catalytic activity of the SCPCs was investigated in the example of liquid-phase hydrogenation of EAA. It was found that the specific activity (SA) of the catalysts, referred to 1 g of catalyst, although it does drop off with increasing Pd content, drops off to a considerably smaller degree than might be expected (see Table 1). In the calculations of the SA referred to  $1 \text{ m}^2$  of Pd, it was found that for the SCPCs with Pd contents of 56.5% and 34.0% (at.), the SA is approximately the same as for the skeletal Pd. This indicates that the observed reaction rate is determined solely by the amount of surface of the active



Fig. 1. Charging curves of SCPCs containing the following amounts of Pd in the metallic phase (%): 1) 5.1; 2) 15.1; 3) 34.0; 4) 56.5; 5) skeletal Pd.



Fig. 2. Atomic ratio H/(Pd + Cu) as a function of Pd content in metallic phase of SCPC.

phase of the catalyst, i.e., the Pd or the Pd-based alloy. In the case of the SCPCs with Pd contents of 5.1% and 15.1% (at.), the SA referred to  $1 \text{ m}^2$  of Pd is much higher than that of the skeletal Pd, by respective factors of approximately 150 and 30. This evidently means either that there is a sharp change in the properties of the active phase itself when the change is made from Pd to the SCPC or that there is an activation of the Cu phase, which begins to manifest hydrogenation capability and hence makes its own contribution to the total rate of reaction. The latter hypothesis is the more probable. Such activation of the Cu can be explained, for example, as a manifestation of the spillover effect, as a result of which we find active hydrogen not only on the Pd surface but also on the Cu surface, which can be initiated in the course of the hydrogen acceptor.

Thus, with small contents of Pd (up to 15 at.%) in the SCPC, the Cu phase and the Pdcontaining phase apparently do not exist independently of each other; their interaction is manifested in the above-noted covering of the Pd-containing phase by copper and in the much higher activity of the catalyst in comparison with that calculated on the basis of additivity. A mutual influence of the Cu and the active phase was also suggested in the study of Cu-Ru catalysts, for which a substantial deviation of the catalytic properties from additivity was found for catalysts containing small amounts of Ru (0.5-2%). In bimetallic systems, evidently, if both components exist completely or preferentially in the form of individual phases, when there is a considerable interfacial area between the two metals, their catalytic and adsorption properties may be changed.



Fig. 3. Optical yield (p) of (-)-ethyl  $\beta$ -hydroxybutyrate as a function of Pd content in metallic phase or SCPC.

Fig. 4. Optical yield of (-)-ethyl  $\beta$ -hydroxybutyrate as a function of pH of modification with R,R-(+)-tartaric acid for SCPC containing 3% (at.) Pd in the metallic phase.

Experiments on the hydrogenation of EAA on SCPCs modified with R,R-(+)-tartaric acid showed that with Pd contents of 5% (at.) or less, they manifest enantioselectivity, which increases with increasing Pd content (Fig. 3). Thus, in addition to the already discussed features for the SCPCs with low Pd contents, we should add their capability for performing asymmetric catalysis. The lack of any enantioselectivity in the SCPCs with relatively high Pd contents is readily explained on the basis that, according to the data we have presented, the active phase has the same composition as the Pd, which is incapable of enantioselective hydrogenation.

In the case of the SCPCs with Pd contents below 5%, the manifestation of asymmetrizing capabilities is consistent with the hypothesis that in these catalysts, along with the Pd, a Cu phase begins to be manifested. Actually, since the Cu can perform the enantioselective hydrogenation of EAA with optical yields (p) up to 17% [4], then, when it manifests its catalytic activity in the SCPCs with low Pd contents, it can make a contribution to the formation of the optically active product. The increase of enantioselectivity upon going from 5% to 1% Pd in the SCPCs is consistent with the above-noted increase of the interaction of phases in the mixed catalysts with decreasing Pd content. Thus, the introduction of 1% Pd into the Cu offers a means for preparing catalysts that are active at 90-100°C, not only at 130-140°C as in [4], and that have enantioselectivities comparable to that of Cu.

The view that the manifestation of optical activity in the products of EAA hydrogenation on SCPCs with low Pd content is due to the appearance of catalytic activity for the Cu is supported to a certain degree by the fact that the dependence of p on the pH of modification for these catalysts is similar in form to the analogous dependence obtained for skeletal copper [4], but the values of p pass through a maximum at pH 7 (Fig. 4).

Thus, these studies of the properties of SCPCs have shown that, because of the way the catalysts are prepared, the Cu and Pd are almost or entirely separated into two phases, the properties of which remain constant over a broad range of Cu/Pd ratios. With small contents of Pd, however, the properties of the SCPCs deviate very markedly from additivity; in particular, asymmetrizing properties appear, and it becomes possible to prepare catalysts for which, even though the enantioselectivity is fairly low, the hydrogenation rates are quite high. The specific hydrogenation rates are quite similar for the skeletal Ru-Cu [4] and Pd-Cu catalysts (310 and 470 mmoles/h per gram of metal, respectively), but the rate of accumulation of the excess (-)-enantiomer is three times as high with the Pd-Cu system (42 vs 13 mmoles/h per gram of metal).

### CONCLUSIONS

1. It has been established that skeletal Cu-Pd catalysts contain phases of Pd and Cu or a Pd-based solid solution, and also Pd, and  $Al_2O_3 \cdot 3H_2O_3$ .

2. The adsorption of hydrogen on these catalysts in a  $0.1 \text{ N} \text{ H}_2\text{SO}_4$  solution has been investigated, and it has been found that the quantity of hydrogen adsorbed on the skeletal copper-palladium catalysts drops off very rapidly as the Pd content in the metallic phase is increased from 5.1% to 15.1% (at.).

3. The possibility of catalytic activation of the copper by the palladium has been demonstrated, and also the capability of the skeletal copper palladium catalysts for performing enantioselective hydrogenation.

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DECOMPOSITION OF HYDROGEN PEROXIDE IN ACETIC ACID, CATALYZED BY VANADIUM COMPLEXES

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The redox reactions of  $H_2O_2$  catalyzed by transition-metal complexes are used extensively in preparative chemistry and also in commercially important processes [1]. The reactions of  $H_2O_2$  in solutions of V complexes, in contrast to its behavior in solutions of Co, Mo, or W complexes, have not been studied adequately [2]. Here we are reporting on an investigation of the decomposition of  $H_2O_2$  in AcOH medium, catalyzed by V complexes; no information whatever has been reported previously on this particular reaction.

## EXPERIMENTAL

The experiments were performed in a 30-ml Pyrex glass reactor equipped with a magnetic stirrer, thermometer, and reflux condenser. During the course of the experiments, samples of the solution were drawn and analyzed iodometrically for total peroxide content. The content of  $H_2O_2$  in the presence of AcOOH was determined by a procedure described in [3]. The following materials were used in the experiments: Perhydrol conforming to the standard GOST 5.547-70 AcOOH prepared by procedures described in [4]; AcOH, chemically pure grade, distilled from  $CrO_3$  in a fractionating column (fraction with bp 117.9-118.1°C at 760 mm); Ac<sub>2</sub>O, pure grade, distilled (fraction with bp 139-140°C at 760 mm).

#### DISCUSSION OF RESULTS

In order to evaluate the influence of uncatalyzed (thermal) decomposition of peroxides in this system, experiments were set up to investigate the kinetics of  $H_2O_2$  consumption in solutions of AcOH without any vanadium compounds.

The addition of crushed quartz (0.03-0.10 mm fraction) to the solution leads to a considerable increase of the peroxide decomposition rate in AcOH medium. The rate of AcOOH decomposition is directly proportional to the amount of quartz added (up to 1% of the AcOH

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