ELECTROCHEMICAL STUDIES ON NOBLE METAL ALLOY CATALYSTS

T. MALLÁT and J. PETRÓ

Department of Organic Chemical Technology,
Technical University, H 1521 Budapest

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Abstract

Hydrogen and oxygen sorption and surface phase composition of noble metal alloy catalysts can be investigated by an electrochemical polarization method. The adaptability of a potentiodynamic polarization method is demonstrated by the study of powdered Pd-Cu and Pd-Cu/C catalysts.

Introduction

Galvanostatic and potentiodynamic polarization has been used for the characterization of noble metal electrodes for a long time. These polarization methods were adopted for the study of powdered noble metal alloy catalysts. Potentiodynamic polarization, which has become predominant of late years, has unique features among catalyst characterization methods; the characteristics of hydrogen and oxygen sorption can be determined from a single curve. With bimetallic catalysts there is a further possibility: from the reduction or dissolution of a few atomic surface layer, surface phase structure can also be determined.

Classical X-ray diffraction fails to prove the existence of surface phases different from bulk ones if their sizes are below about 5 nm. Spectroscopic methods (XPS, UPS, Mössbauer spectroscopy etc.) are widely used for studying surface phases [1]. Electrochemical polarization is also an excellent method for this purpose: it is unsensitive to the size of a phase and gives information about the free enthalphy differences of surface phases. The limitation of the method is the good electric conductivity required: only metal and carbon or graphite supported metal catalysts can be studied. The applicability of potentiodynamic polarization will be shown in the study of Pd-Cu and Pd-Cu/C catalysts.

Experimental methods

The preparation methods of Pd-Cu and activated carbon supported Pd-Cu catalysts have been published earlier [2, 3].

The cell and electrochemical polarization equipment used in the experiments have been described elsewhere [4].

Results and discussion

The potentiodynamic curves for a Pd catalyst and for Pd-Cu catalysts prepared by simultaneous reduction are shown in Fig. 1. In the hydrogen region (below 0,3 V) there are two characteristic maxima on the curve of Pd. The first, large peak is attributable principally to the ionization of hydrogen dissolved in the β-phase, the second pertains to strongly bound, mainly

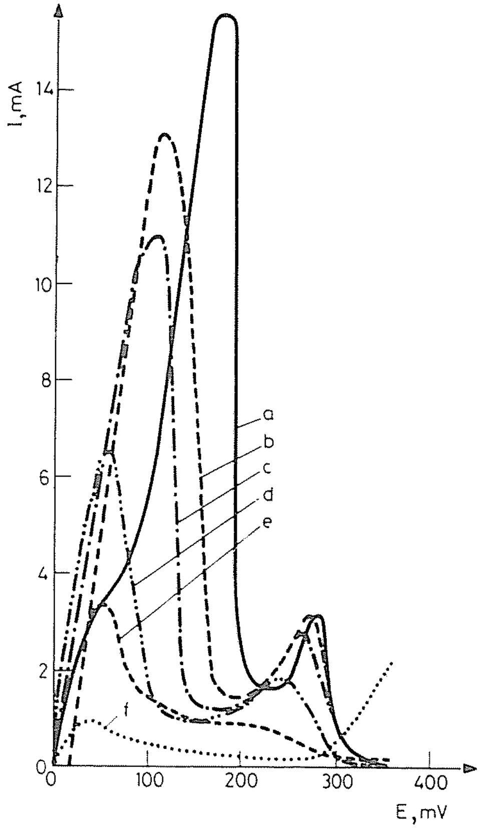

Fig. 1. Potentiodynamic curves of Pd-Cu catalysts ($v = 40$ mV min^{-1}); a) Pd; b) 10 at%Cu-Pd; c) 20 at% Cu-Pd; d) 30 at% Cu-Pd; e) 40 at% Cu-Pd; f) 60 at% Cu-Pd

adsorbed hydrogen [5]. Further maxima can be observed when the sweep rate is kept low [6]. Alloying Pd with increasing amounts of Cu, the amounts of both the absorbed and adsorbed hydrogen decrease, as well as the energy of metal-hydrogen bond (the maxima are shifted gradually toward lower potentials, Table 1).

Table I

Hydrogen contents and locations of maxima on the potentiodynamic curves of Pd-Cu catalysts

Cu atom %	Hydrogen cm^3/g catalyst		Hydrogen ionization maxima (mV)		
	total	loosely bonded			
0	73.1	62.9	64.	175.	258
10	66.5	52.3	46.	—	246
20	51.0	37.8	35.	—	238
30	29.3	19.3	18.	—	220
40	16.9	10.3	—		
60	2.9	—	—		

Plotting the atom ratio of hydrogen dissolved in the β-phase to all metals as a function of copper concentration, the points fall on a single line to a good approximation (Fig. 2). The line intersects the abscissa at a copper content where the dissolution of hydrogen terminates (44 at %). From the quasi-equilibrium peak potentials (E) determined at relatively low sweep rates the free enthalphy change of the $\beta \rightarrow \alpha$ phase transition can be determined by means of equation $\Delta G = -ZFE$. Plotting these values against the copper content, again a straight line can be obtained which intersects the abscissa at 42 at %. The values obtained by the two methods for the limit of β-phase dissolution of hydrogen are in excellent agreement.

In the case of Pd-Cu alloys (and for some other noble metal-non-noble metal alloys, such as Pd-Hg [7], Pd-Co [8] of Pd-Pb [9], the structure of the surface phases can be determined from the anodic branch of the polarization curve, from the dissolution of the surface layer. Figure 2 shoes the potentiodynamic curves of Pd-Cu/C catalysts prepared by reduction of Cu onto a Pd/C catalyst. The peak observed for the samples of low Cu content at ca. 0.5 V can be attributed to the dissolution of a $PdCu_3$ compound phase [10]. With increasing Cu content the amount of this phase increases and according to the above said, the change in hydrogen sorption indicates that a Pd-rich, homogeneous alloy is also formed. From a copper content of 30 at %, unalloyed Cu is also present on the surface: the peak of the dissolution of Cu starts below 0.3 V($E^0_{Cu/Cu^{2+}} = 0.34$ V). In parallel, hydrogen sorption decreases to a minimum. This method could be used, therefore, to show that in the reduction of Cu onto Pd 3 different Cu-containing phases were formed.

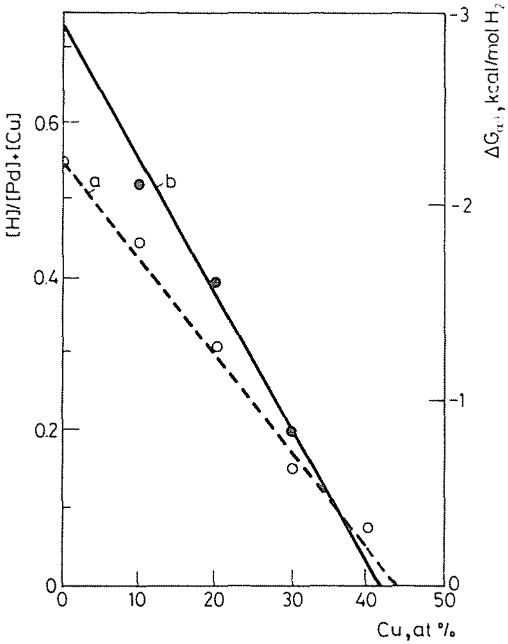

Fig. 2. Dissolution of hydrogen in Pd-Cu catalysts (a), and free enthalphy change of hydrogen dissolution as a function of the composition (b)

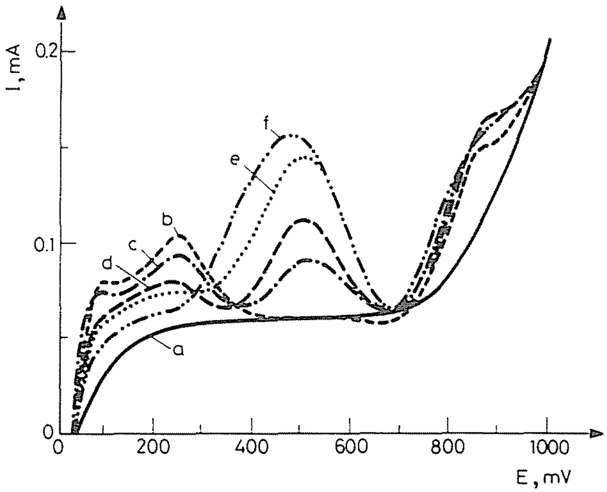

Fig. 3. Potentiodynamic curves of Pd-Cu/C catalysts, a) activated carbon support; b) Pd/C; c) 10 at% Cu-Pd/C; d) 20 at% Cu-Pd/C; e) 30 at% Cu-Pd/C; f) 40 at% Cu-Pd/C

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Dr. Tamás MALLÁT } H—1521 Budapest
Dr. József PETRÓ }