

## Relationship Between the Activity and the Excess Free Surface Energy of Noble Metal Catalysts

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The relationship between the excess free surface energy ( $\Delta F$ ) of noble metal catalysts (Pt, Pd, Ru, and Ir), prepared by various methods, and their catalytic hydrogenation activity has been investigated.

The excess free surface energy was determined by the measurement of the electrochemical potential of the degassed powder catalysts. The potential of the catalysts was measured in a 1 *N* HCl solution,  $10^{-3}$  *M* with respect to its own ions, referred to the Ag/AgCl/HCl reference electrode.

It has been established that *for a given metal* there exists a relationship between the different activities, depending on the mode of preparation and the free energy values; notably, higher activities correspond to larger excess free energies.

The excess free surface energy of the *various metals* is characteristic primarily of the nature of the given metal. On comparing the excess free surface energies of various metals, a higher excess in free energy does not mean at the same time a higher catalytic activity, but a relationship was found between  $\Delta F$  and the heat of sublimation.

### INTRODUCTION

The catalytic properties of a given substance are determined by two fundamental factors: the nature of the substance and the mode of preparation. The problem, how and to what degree the catalytic properties of the solid substance can be changed by the mode of preparation, as compared to the substance in thermodynamic equilibrium, has been much debated and is still not clear. According to the most generally accepted view, catalysts are assumed to be substances with excess free energy which are not in a thermodynamically stable state. Their excess free energy is accumulated during their preparation. The increase in free energy ( $\Delta F$ ) is represented by the following equation (1-3):

$$\Delta F = F_{\text{act}} - F_{\text{min}}$$

where  $\Delta F$  is the excess free energy of the solid substance,  $F_{\text{act}}$  is the free energy of the active solid substance (catalyst), and

$F_{\text{min}}$  is the free energy of the solid substance in the thermodynamically stable state.

The *excess* in free energy of solid substances can be ascribed essentially to the following causes:

1. Atomic lattice defects, irregular crystal growth, inhomogenous density.
2. Incorporation of foreign molecules, atoms, solid particles in the lattice.
3. The presence of a (nonequilibrium) phase, which under the given conditions does not figure in the phase diagram.
4. Increase in dispersity.

The increased free energy influences the physical and chemical properties of the solid substance, e.g., the electrochemical potential, the catalytic activity, sorption ability, the electrical conductivity, the specific heat, equilibrium and kinetics of chemical reactions, etc. It is a generally accepted concept that catalysts are substances with *excess* free energy. However,

the reverse is not valid, that is to say, not all the substances with excess free energy are at the same time catalysts. One of the reasons for this is that only certain kinds of excess free energy are associated with the catalytic properties, and in addition only a part of the excess free energy is at the surface. From the point of view of catalysis, the excess free energy at the surface is the most important, and it is evidently not independent of the total excess in free energy of the solid substance.

The final aim of our research work is to characterize hydrogenation-dehydrogenation metal catalysts independently from their catalytic reactions. Within the scope of this work, the relationship between the excess free surface energy and the catalytic properties of a few metals have been studied. Of the properties changing with the excess free energy, we have chosen to measure electrochemical potential,<sup>1</sup> since this reflects the excess free surface energy ( $\Delta F$ ), important from the point of view of catalysis.

By the measurement of  $\Delta F$  on the basis of the electrochemical potential, Hüttig (1, 7) and others (4-6) demonstrated the difference in free energy between compact metals and metal powders, and studied poisoning phenomena. The number of the investigations from that time is rather scarce, and measurements are not sufficiently accurate from the point of view of electrochemistry. The authors arrived at the conclusion that the excess free energy can be measured, but they did not find or even investigate relationships with the catalytic properties.

## EXPERIMENTAL

### Experimental Methods

Valuable work was carried out by Roginskii *et al.* (3), who measured the free surface energy of catalysts, primarily of oxides, while Hüttig (1, 7) examined this theme in general. However, such methods

<sup>1</sup> Strictly speaking, the measured  $E$  are not real "electrochemical potentials" (i.e., equil. emf) but rather "zero-current potentials."

are not widely used, and knowledge in this field is still rather inadequate.

The excess free surface energy ( $\Delta F$ ) of metals is normally measured by an electrochemical method in which two metal sheets, which are in thermodynamic equilibrium (there is no potential difference between the sheets) are immersed in a solution of their own ions. One of the sheets is in contact with the metal to be measured, having excess free surface energy, while the other sheet is in contact only with the solution. A potential difference ( $E$ ) is established between the two sheets, from which the excess free surface energy can be calculated with the following formula:

$$\Delta F = n \cdot 23060 \cdot E \text{ (cal/mole),}$$

where  $n$  is the valency of the metal ions in the solution, and  $E$  is the potential difference in volts, measured between the two sheets.

The excess free surface energy measured in this way is integral, which obviously makes impossible a finer analysis. Moreover, it involves the assumption that the surface energy state of the solid substance does not change during the measurement.

Measurements of the excess free surface energy were begun by us using the above method. However, it was found to be too cumbersome. It is rather complicated to prepare thermodynamically stable metal pieces, and also the attainment of zero potential difference between the two metal pieces is in general a slow process, requiring a period from a few hours to a few days; moreover, results cannot be well reproduced. Therefore, a measuring method was developed which gave within a relatively short time reproducible results. This method is described below.

The cell used is shown in Fig. 1. The platinum electrode (2, Fig. 1) serves only as a terminal; it takes up the potential of the catalyst, but has no other role. Therefore, stable Pt, easy to clean, was used for this purpose. As reference electrode (5, Fig. 1) the system Ag/AgCl/HCl with a well-defined potential has been selected. To reduce to a minimum the diffusion potential, an identical Cl<sup>-</sup> ion concentration

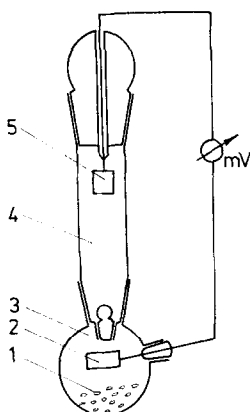


FIG. 1. Apparatus for the measurement of excess free surface energy. 1—Me catalyst; 2—Pt electrode; 3— $\text{Me}^{n+}$  electrolyte; 4—HCl solution; 5—Ag/AgCl electrode.

(1 *N*) was established in the upper and the lower electrode zones, and with the same purpose a small metal ion concentration ( $10^{-3}$  mole/liter) was selected for the lower electrode zone.

If the object is the measurement of the excess free surface energy of the metal, hydrogen sorbed on the metal must be removed before the measurement, and this was not done in earlier measurement. This is necessary for two reasons. On the one hand, metal catalysts with hydrogen at their surface can be considered in general as mixed catalysts. In the case of noble

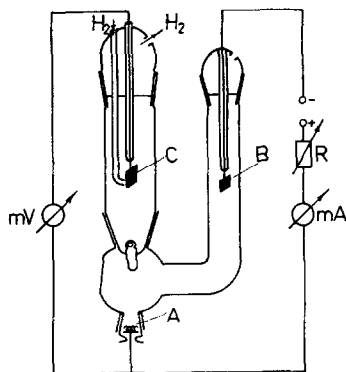


FIG. 2. Polarizing apparatus. A—polarizing Pt sheet, holding the catalyst; B—polarizing auxiliary electrode, Pt sheet; C—platinized platinum hydrogen electrode.

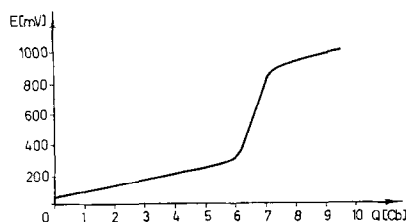


FIG. 3. Charge curve of Pt catalyst (1 *N* sulfuric acid, 100 mg of catalyst,  $i = 1.5$  mA).

metals (the potential of which is more positive than that of hydrogen), the potential is determined by the less noble hydrogen. On the other hand, active hydrogen at the surface of the metal will reduce the metal ions in the contacting solution, so that the concentration of the solution will change uncontrollably, and consequently also the potential and, due to separation of metal, the surface of the catalyst.

Adsorbed hydrogen has been removed from the catalyst in the apparatus shown in Fig. 2, by anodic polarization up to a definite potential value. The appropriate polarization values have been determined by recording the charging curves of the single catalysts. For this purpose, 30–100 mg of catalyst has been anodically polarized in 1 *N* sulfuric acid with a current of 1.5 mA, and the change in potential has been plotted as a function of the charge quantity. Charging curves are shown in Figs. 3–6. The initial flat section of the curves corresponds to the desorption of hydrogen from the catalyst, the next steep section is the so-called double-layer region, in which the quantity of absorbed charge is used only for the formation of the

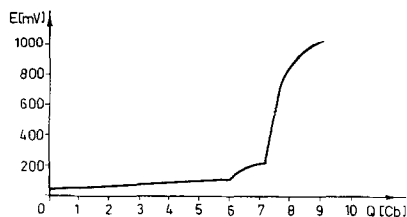


FIG. 4. Charge curve of Pd catalyst (1 *N* sulfuric acid, 100 mg of catalyst,  $i = 1.5$  mA).

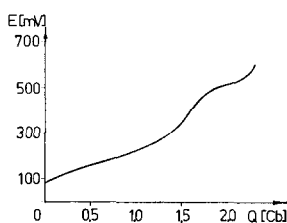


Fig. 5. Charge curve of Ir catalyst (1 *N* sulfuric acid, 50 mg of catalyst,  $i = 150 \mu\text{A}$ ).

double-layer, and this is followed by the almost horizontal section, in which the adsorption of oxygen begins. The surface of the catalyst can be considered only in the double-layer region as gas free, so that polarization was carried on up to a potential corresponding to the central part of this region, i.e., in the case of Pt and Pd up to 500 mV, while in that of Ru and Ir up to 350 mV. It was verified that the excess free energy of the catalysts is identical along a region differing by  $\pm 100$  mV from the above potential values. Thus, it can be accepted that the potential is determined during measurement by the surface of the catalyst, in contact with its own ions.

The catalyst degassed in this way has been placed into the lower vessel of the free energy measuring apparatus (Fig. 1), and five glass beads of 1–2 mm diam have been added to ensure mixing. Next, the vessel has been filled up on air-bubble-free  $10^{-3} M$  solution of the catalyst metal ions, which was 1 *N* with respect to HCl. Pure 1 *N* HCl solution was poured into the zone of the upper electrode, and the freshly prepared Ag/AgCl electrode was placed into this solution. Shaking the apparatus at a speed of 330 vibrations/min, the potential

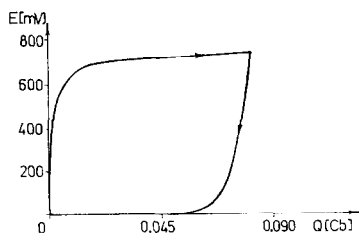


Fig. 6. Charge curve of Ru catalyst (1 *N* sulfuric acid, 50 mg of catalyst,  $i = 1.5 \text{ mA}$ ).

was read at intervals of 5–15 min. The measurement was considered as terminated when the potential value remained constant over several hours. The excess free surface energy was calculated from the potential values obtained.

Measured as described above, the  $\Delta F$  value of a given catalyst does not depend either on the quantity of the catalyst or on the speed of shaking of the glass vessel, but is a reproducible value (measuring error is within 5%), characteristic of the mode of preparation of the catalyst.

#### Catalysts

From the metals investigated, catalysts were prepared in general by the following four methods.

**1. Reduction with formaldehyde.** To a 10% metal chloride solution containing 5 g of metal, 50 ml of 40% formaldehyde was added. Under intensive stirring, a solution of 40 g NaOH in 50 ml of water was added dropwise during 1 hr to the mixture. The temperature of the solution was raised to 60°C, and the solution was kept for 15 min at this temperature. The catalyst was then filtered off, washed with hot distilled water to constant potential, and dried in a vacuum desiccator at room temperature to constant weight.

**2. Hydrogenation at atmospheric pressure.** The pH of a 10% metal chloride solution, containing 2 g of metal, has been adjusted with 20% NaOH to 5–6 pH and, under shaking, the solution was hydrogenated at room temperature and 1 atm pressure. The catalyst separating has been washed with hot distilled water to constant potential, and dried in a vacuum desiccator at room temperature to constant weight.

**3. Reduction with sodium borohydride.** A 10% metal chloride solution containing 2 g of metal was diluted to about 1000 ml and, under stirring, reduced at 20°C with a solution of 4.5 g of NaBH<sub>4</sub> in 50 ml of water. (Sodium borohydride was added slowly, dropwise.) The catalyst separating was filtered, washed with distilled water to constant potential, and dried in a vacuum desiccator at room temperature to constant weight.

**4. Adams' method.** A 10% metal chloride solution, containing 2 g of metal, and 4 g of  $\text{NaNO}_2$  were placed into a porcelain dish, and mixed with 10 ml of water. Stirring with a glass rod, the substance was heated until the water was evaporated. Continuing heating, the mixture was fused, and nitrous vapors were liberated. After the stopping of gas evolution, the melt was allowed to cool, and 50 ml of water was added. The precipitate was filtered off, washed with hot water to constant potential, and dried in a vacuum desiccator at room temperature to constant weight. The metal-metal oxide mixture formed was reduced with hydrogen in the liquid phase, at atmospheric pressure and room temperature.

#### RESULTS AND DISCUSSION

Our work had a triple object:

(i) to develop a reproducible measuring method for the measurement of the  $\Delta F$  of metal powder catalysts;

(ii) to find a relationship between  $\Delta F$  and the catalytic activity, and

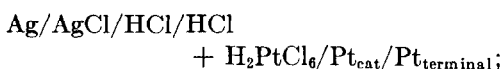
(iii) to find a relationship between  $\Delta F$  and the nature of the metal.

For each metal, catalysts with different antecedents, prepared by four methods, were available for our investigations. The excess free surface energy of the catalysts and their hydrogenating activity have been measured.

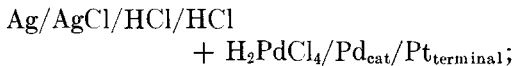
In the hydrogenation experiments, eugenol, nitrobenzene, and acetone were used as reactants, with absolute alcohol as solvent. Activity is given as the quantity of hydrogen (in milliliters) consumed from the gas zone at room temperature in 1 min, referred to 1 g of the catalyst.

The excess free surface energy of Pt, Pd, Ru, and Ir catalysts has been determined by this method on the following electrochemical systems:

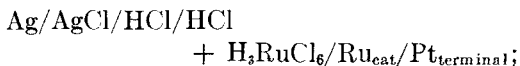
In the case of Pt,



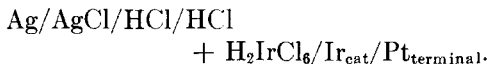
In the case of Pd,



In the case of Ru,



In the case of Ir,



The electromotive force measured is

$$E_m = E_2 - E_1,$$

where  $E_1$  is the potential of  $\text{Ag/AgCl/HCl}$ , and  $E_2$  is the potential of the catalyst. If the potential of the catalyst ( $E_2$ ) is calculated from this formula, and the potential of the metal in thermodynamically stable state is determined with the Nernst formula ( $E_{\text{calc}}$ ), the potential difference proportional to  $\Delta F$  ( $E$ ) can be obtained as the difference of the two values:

$$E = E_{\text{calc}} - E_2.$$

From the  $E$  value obtained as described above,  $\Delta F$  values calculated with the formula  $\Delta F = n \cdot 23060 \cdot E$  are contained in Table 1.

TABLE 1  
EXCESS FREE SURFACE ENERGY OF  
NOBLE METAL CATALYSTS

Catalyst	Mode of preparation	Excess free surface energy (kcal/mole)
Pt	Red. with $\text{NaBH}_4$	1.52
	Red. with $\text{H}_2$	4.01
	Red. with HCHO	4.98
	Adams' method	6.32
Pd	Red. with $\text{NaBH}_4$	1.25
	Red. with $\text{H}_2$	1.53
	Red. with HCHO	2.08
	Adams' method	2.36
Ru	Red. with HCHO	6.60
	Adams' method	8.30
	Red. with $\text{NaBH}_4$	15.60
Ir	Red. with $\text{H}_2$	14.70
	Adams' method	19.80
	Red. with $\text{NaBH}_4$	24.00

TABLE 2  
THE ACTIVITY OF NOBLE METAL CATALYSTS IN THE HYDROGENATION OF ACETONE, EUGENOL,  
AND NITROBENZENE AT ROOM TEMPERATURE

Catalyst	Mode of preparation	Activity (ml H <sub>2</sub> /min g of catalyst)		
		Acetone	Eugenol	Nitrobenzene
Pt	Red. with NaBH <sub>4</sub>	—	44	34
	Red. with H <sub>2</sub>	—	95	73
	Red. with HCHO	—	113	121
	Adams' method	—	206	320
Pd	Red. with NaBH <sub>4</sub>	—	62	—
	Red. with H <sub>2</sub>	—	77	—
	Red. with HCHO	—	100	—
	Adams' method	—	121	—
Ru	Red. with HCHO	5	2	—
	Adams' method	8	5	—
	Red. with NaBH <sub>4</sub>	17	12	—
Ir	Red. with H <sub>2</sub>	—	1	2
	Adams' method	—	14	17
	Red. with NaBH <sub>4</sub>	—	34	50

The activities of the catalysts are summarized in Table 2. Values obtained show that for each of the metals an activity interval is given, associated with the mode of preparation, and the magnitude of this interval depends also on the nature of the metal. Platinum has the highest activity (its activity range is 34–320 ml H<sub>2</sub>/min g), while ruthenium has the lowest activity (activity range 2–17 ml H<sub>2</sub>/min g).

According to our experiments, the excess free surface energy, as with the activity, depends strongly on the mode of preparation. The ratio of the highest and lowest

$\Delta F$  values varies on a metal between 2 and 4. It can be established, however, that the numerical value of the free energy of a given metal is determined primarily by its nature, and this value is influenced within given limits by the mode of preparation. Ir has the highest  $\Delta F$  (14.7–24 kcal/mole), and Pd the lowest (1.25–2.36 kcal/mole).

When the free energy values contained in Table 1 are plotted as a function of activity (Figs. 7–10), a relationship between activity and  $\Delta F$  is obtained, which implies that on a given metal the catalyst of higher activity has the larger excess free energy. This relationship shows in the case of Ru a direct proportionality (Fig. 7),

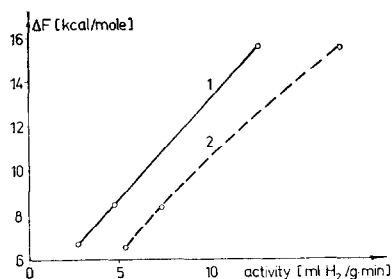


FIG. 7. Relationship between the activity and the excess free surface energy of Ru catalyst with 1—eugenol, 2—acetone.

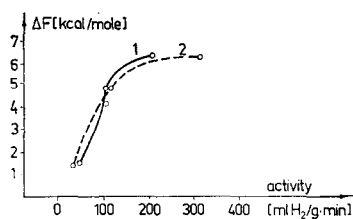


FIG. 8. Relationship between the activity and the excess free surface energy of Pt catalyst with 1—eugenol, 2—nitrobenzene.

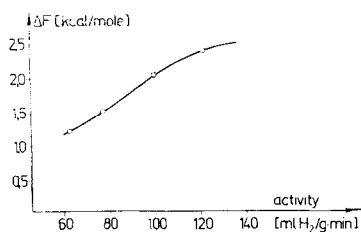


FIG. 9. Relationship between the activity and the excess free surface energy of Pd catalyst, measured with eugenol.

while in the case of the other metals (Pt, Pd, Ir) the curves become flatter in the direction of higher activities (Figs. 8–10).

The change in activity caused by a unit change in  $\Delta F$  on each metal can be established by considering the straight sections of Figs. 7–10. These data are given in Table 3. The picture which can be formed on the basis of this table is consistent with the experience that, the higher the activity of a catalyst, the greater is its sensitivity to the mode of preparation.

When the activity and the excess free surface energy of various metals is compared, it is no longer true that a higher activity corresponds to a greater  $\Delta F$ ; indeed, it has already been indicated that the value of the free energy is determined by the nature of the substance.

In the search for a relationship between the nature of the substance and  $\Delta F$ , the relationship between  $\Delta F$  and a surface characteristic of the metal, the heat of sublimation, has been investigated (Fig. 11). It was found that, the higher the heat

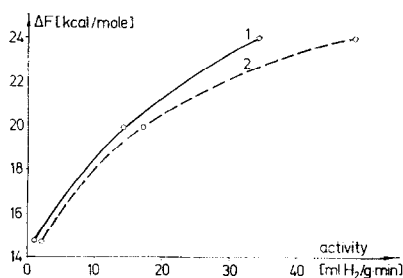


FIG. 10. Relationship between the activity and the excess free surface energy of Ir catalyst with 1—eugenol, 2—nitrobenzene.

TABLE 3  
EFFECT OF THE UNIT CHANGE IN THE  $\Delta F$  VALUE OF CATALYSTS ON THEIR ACTIVITY ( $A$ )

Catalyst	$(\Delta F)$	$A$	$\frac{\Delta A}{\Delta(\Delta F)}$
Pt	3.5	70	20
Pd	0.8	40	50
Ir	5.1	12	2.4
Ru	9.0	10	1.1

of sublimation (i.e., the bond strength of the surface metal atoms in the lattice), the greater is the excess free surface energy. Thus, there seems to be a correlation between  $\Delta F$  and a parameter characteristic of the nature of the substance, namely, the bonding strength of the surface metal atoms.

Finally, it should be mentioned that factors which may influence the accuracy of the measurement, or rather, which do not make possible work under scientifically "pure" conditions, include instability of the catalysts, incomplete purity of the surface of a "living" catalyst, and also the very weak currents which pass through the catalyst during the measurement and which may change the structure of the solid. Similarly, there is no way to measure the  $\Delta F$  of the different active centers, as only average values are obtained on the surface. In spite of this, the measurement of  $\Delta F$  seems to be useful in the evaluation of catalysts, as one characteristic among several others, because it reflects on the one hand the nature of the substance, and on the other hand the effect of the mode of preparation, so that it yields valuable informations on one of the sources of catalytic properties.

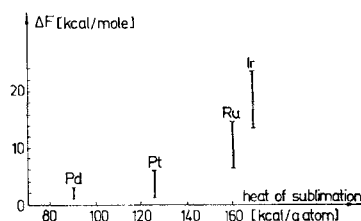


FIG. 11. Relationship between the heat of sublimation and the excess free surface energy.

## CONCLUSIONS

1. A measuring method, reported in the literature of the thirties, but completely neglected since then, has been brought up to date and adapted to noble metal catalysts, to measure with good reproducibility the excess free surface energy.

2. It has been established that the excess free surface energy varies within more or less broad limits in dependence on the mode of preparation, and, moreover, is a function of the nature of the substance.

3. For a given metal, the higher the excess free surface energy, the higher the catalytic activity in hydrogenation. However, a higher  $\Delta F$  value for another metal

does not mean of necessity a higher catalytic activity, because the free energy depends in essence on the nature of the metal and on the strength of the metal-metal bonds.

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