

ELECTROCATALYSIS AND HYDROCARBON OXIDATION

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EXTENDED ABSTRACT

An attempt is made to correlate the catalytic activities and physical properties of noble metal electrocatalysts, using ethylene oxidation at 80°C, in 1 N sulfuric acid as a test reaction. Relative catalytic activities are measured by a comparison of current values at an arbitrarily chosen potential.

A correlation was found between catalytic activity and both Latent Heat of Sublimation of the metal (L_s), which according to Pauling's formula reflects the adsorbate-adsorbent bond strength, and also the number of unpaired "d" electrons in the metal. Both of these parameters gave a "volcano" type relationship, when plotted against reaction rate.* (Figs. 1 and 2)

In both cases, Pt lay at the peak of the curve. Values of L_s for alloys were computed by assuming additivity of the L_s values of the components. Values of n_d , the number of unpaired "d" electrons, were obtained by using the values obtained for the first Period of Transition metals, and again assuming additivity in the case of the alloys.

In order to interpret the above relationships, the diagnostic criteria for mechanism determination were examined, and information on adsorption of ethylene was obtained elsewhere.¹ The results are shown in Table 1, A and B.

Oxygen coverage on the noble metals has been shown² to be proportional to the number of unpaired "d" electrons, and similar behaviour might be expected for ethylene. Thus on Gold, ethylene is known to be very slightly adsorbed¹, while on Platinum, the saturation coverage is that amount that might be predicted on the basis of 0.55 "d" electrons per Pt atom³. The apparent weak adsorption of ethylene on Rhodium, appears to result from competitive adsorption with oxygen, which is known to adsorb more strongly on this metal than on Pt⁴. The presence of less than 10% oxygen coverage is known to inhibit adsorption of organic species⁵.

* The almost identical behaviour of Au and Pd (see Table I A) suggest that under the conditions of the experiment, hydrogen or hydrogen containing species are absorbed in the Pd, thus filling the "d" band vacancies.

Table I A

Metal	Tafel Slope (mv)	i_{600}	$\frac{d \log i}{dP_{eth}}$	$\frac{d \log i}{dP_H}$	Reaction Products
Platinum	140	5×10^{-6}	-0.2	0	CO ₂
Palladium	190	2×10^{-7}	+0.5	0*	50% CO ₂ balance aldehydic
Rhodium	160	1×10^{-7}	+0.5	0	CO ₂
Iridium	160	3×10^{-7}	+0.5	0	CO ₂
Gold	200	2×10^{-7}	+0.5	0*	As Pd
Osmium	--	$< 1 \times 10^{-8}$	+ ?	--	--
Ruthenium	165	1×10^{-7}	+ ?	--	--
Silver	--	5×10^{-8}	+ ?	--	--
Mercury	--	$< 1 \times 10^{-8}$	+ ?	--	--

i_{600} denotes current at 0.6 volts vs R.H.E.

0* denotes that pH effect was zero in the range pH = 0 to 4.0. The reaction did not appear to proceed in alkaline solutions

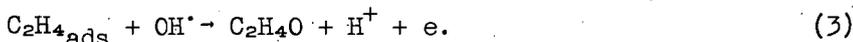
-- denotes parameter not measured due to experimental difficulties

+ ? denotes positive pressure effect of unknown magnitude

Table I B

Alloy	Tafel Slope	i_{600}	$d.i/d.P_{eth}$
Pd-Au 20-80 At% 46-54 At% 78-22 At%	2RT/F	6×10^{-7} 3×10^{-7} 4×10^{-7}	+ve \sqrt{p}
Rh-Pd 25-75 At% 50-50 At% 75-25 At%	2RT/F	7.0×10^{-7} 1.5×10^{-6} 3.0×10^{-6}	+ve
Cu-Rh 10-90 At%	2RT/F	4.0×10^{-6}	+ve \sqrt{p}
Cu-Au 25-75 At%	—	1×10^{-7}	—
Pt-Ru 80-20 At% 50-50 At%	2RT/F	8×10^{-7} 5×10^{-7}	+ve
Pt-Ni 85-15 At%	2RT/F	4.0×10^{-7}	—

In the case of Platinum, previously described by⁷, the following mechanism was suggested,



where step (2) was rate determining. This mechanism is obviously not applicable to other metals, where a positive fractional order of reaction with respect to ethylene indicates that an adsorbed organic species is involved in the rate determining step. In order to interpret the observed empirical rate equation:

$$i = k e^{\frac{FV}{RT}} p^{1/n} c_{\text{H}^+}^{-0.5} \quad (1)$$

Two mechanisms are proposed.

I. Radical Attack

In this mechanism, the sequence suggested above still applies, except that step (3) is now rate determining. Such a mechanism would give rise to an equation such as the above if coverage with OH[·] or O[·] were to change linearly with potential, as is often the case. The change of rate control from step (3) in the case of Au to step (2) for Pt and back to (3) for Rh, and the various factors controlling it, are considered in Table II.

TABLE II

Parametric Change	Forward Rate of (2)	Forward Rate of (3)
Increase in θ_{OH}	decreases	increases
Increase in θ_{eth}	decreases	increases
Metal-OH bond strength	increases	rises to max, then decreases.
Metal-ethylene bond strength	—	rises to max, then decreases.

Thus an optimum value exists, lying between the extremes of weak adsorption (not true chemisorption) and strong adsorption (immobile species, metal-adsorbate bond hard to break). The rate of step (3) will be highest on catalysts with high coverages of both adsorbed species, and intermediate values of bond strengths. It seems that Pt fulfills these conditions, having however a relatively slow rate for step (2) owing to the high coverage of ethylene.

This accounts for step (2) being rate determining. On gold, very low coverages and low bond strengths of adsorbed radicals result in step (3) proceeding slowly. The same is true on Rhodium, again because of very low ethylene coverage but also because of the much higher Metal-Oxygen bond strength. In both cases, step (3) becomes rate determining. The weakness of the Metal-Organic chemi-bond in the case of gold, is the probable reason for desorption of intermediates such as aldehydes, as opposed to the complete oxidation to CO₂ observed on other metals.

II. Electron Transfer from Organic Species

In this second possible mechanism, which has already been proposed for many oxygen containing organic species (6), the sequence is:



Such a mechanism is possible whenever zero or positive pressure effects with respect to concentration of organic species are observed.

An attempt to distinguish between mechanisms I and II is presently under way, involving H/D isotope effects.

References

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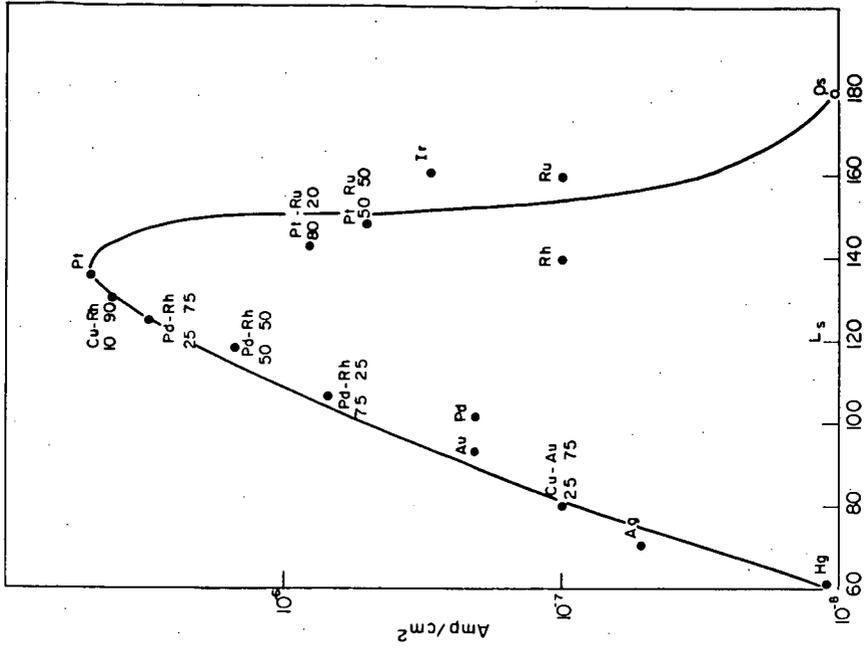


Fig. 2.-EFFECT OF LATENT HEAT OF SUBLIMATION ON CATALYTIC ACTIVITY

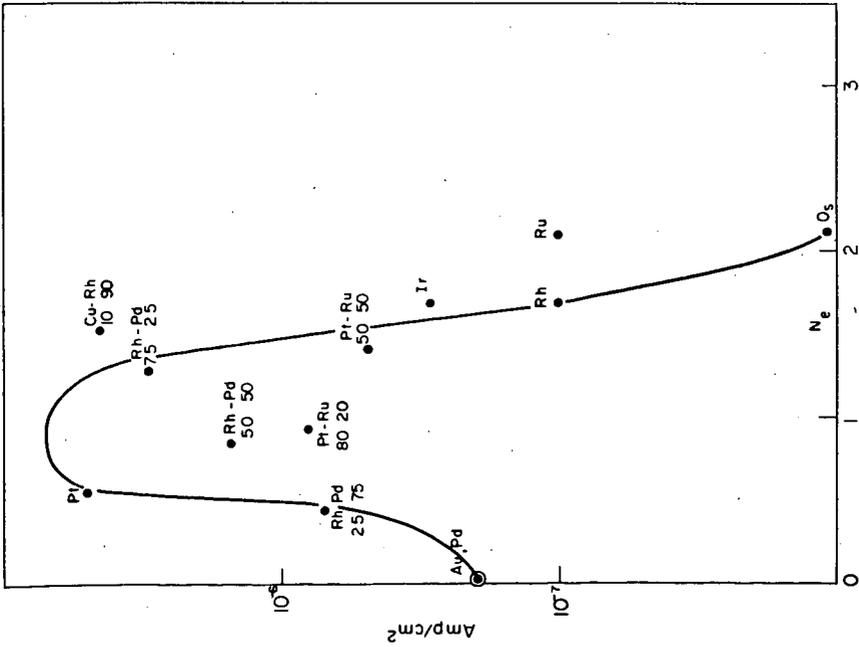


Fig. 1.-EFFECT OF UNPAIRED d ELECTRONS ON CATALYTIC ACTIVITY