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The Electrical Conductivity of Supported Metal Catalysts

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Studies of the electrical conductivity of supported metal catalysts, Rh, Pt, Ru, Pd on Al_2O_3 and SiO_2, has revealed that the systems behave as semiconducting systems either electronic, or protonic in nature. At temperatures between 50 and 350°C, log conductivities against $1/T$ yield straight line plots with corresponding activation energies between 8 and 27 kcal $mole^{-1}$. The activation energies for conductivity are comparable with activation energies for some catalytic reactions. The implications for catalysis are discussed.

INTRODUCTION

In 1969, R. M. Hill (*1*) published a paper on electrical conduction in discontinuous metal films. These films were ultrathin and were composed of discrete particles of metal, gold, platinum, or chromium, deposited from vapor on to glass substrates. The initial deposits were highly discontinuous, yet these were found to be electrical conductors. The conductivity was less than that expected for an equivalent plane and parallel foil of the metal, and the temperature coefficient of the resistance was like that of a semiconductor.

When the logarithm of conductance was plotted against reciprocal temperature, straight line regions were found which defined an activation energy for conduction, specifying the height of the potential barrier over which charge was thermally excited.

From the point of view of catalysis, the systems investigated by Hill (*1*) and others (*2*) bear a close resemblance to supported-metal catalyst systems. They both involve metal particles dispersed upon insulating supports. It was, therefore, of immediate interest to see if the activation energies for conduction of this kind were in the regions observed in catalytic conversions: In fact, the activation energies for conduction recorded by Neugebauer and Webb (*2*) were between 0.18 and 0.64 eV for platinum on glass: These are comparable with activation energies found for some catalytic processes.

Thus it was decided that an attempt should be made to measure the activation energies for conduction in supported noble metal catalysts. The ultimate hope was that this might represent the measurement of a physical characteristic of a catalyst which was directly related to a catalytic process.

EXPERIMENTAL

Conductivity

A sensitive vibrating reed electrometer EKCO N616B was chosen for current measurement: a variable dc voltage, 0-2 kV EKCO N529C, was used to apply potential to the Pyrex conductivity cell. This gas-tight cell is shown in Fig. 1.

The temperature in the catalyst bed was measured by a chromel-alumel thermocouple connected to a Comark Electronic Thermometer, 1602. This thermocouple system was electrically isolated from the current-measuring system. As a precaution against surface-leakage currents, a guard ring was incorporated in the glass conductivity cell so that no electrical path existed between the upper and lower electrodes, other than through the catalyst specimen.

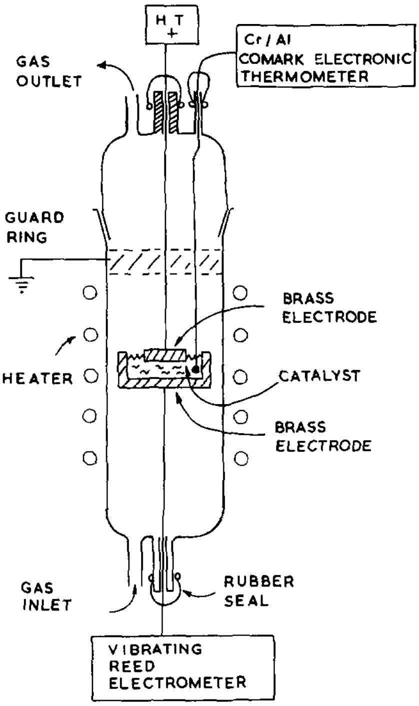

Fig. 1. Conductivity cell.

Catalyst Specimens

These consisted of noble metal on Degussa Aerosil silica or Peter Spence Type A alumina supports. They were prepared by impregnating the carriers with solutions of H_2PtCL_6, or $PdCl_2$, or $RhCl_3$. These were dried at 120°C for 16 hr before being crushed to a fine powder. A commercial catalyst was also used.

Gases

Cylinder nitrogen and hydrogen were dried by passing them through Linde 5A molecular sieve, cooled in liquid nitrogen.

Procedure

Care was taken to ensure that conductivities were measured only of dried samples. Unreduced catalysts were dried at ~300°C for 1–2 hr in a flow of dry nitrogen. Reduced catalysts were obtained by passing dry hydrogen over the catalysts for 3–4 hr at 350°C. The hydrogen stream was usually replaced by a flow of nitrogen for conductivity measurements.

The catalyst specimens were heated at 350°C in a flow of dry nitrogen and the applied voltage adjusted for full-scale readings on the vibrating reed electrometer. Heater current was switched off when readings were taken, otherwise ac pickup interfered with measurements.

A series of measurements of current against a fixed applied voltage was then made.

RESULTS

Since the mV output of the electrometer was proportional to conductivity, the results have been presented as log (mV) vs $1/T$: activation energies for conductivity could thus be calculated. Currents measured varied between 10^{-8} and 10^{-11} amp, for temperatures between about 200 and 80°C.

A typical plot is shown in Fig. 2. Repeat measurements gave consistent activation energy values. Log plots for conductivity measured when temperature was falling were identical with those for rising temperature. Electrode contact with the catalysts was difficult to make, thus quantitative determinations of specific conductivity were not possible. Once established, it was

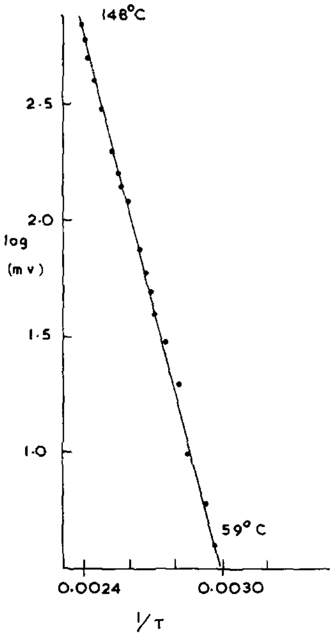

Fig. 2. Plot of log (mV) vs $1/T$ (K) for 5% $Rh-Al_2O_3$. Applied voltage 150 V. Head resistor 10^8 ohm: Readings 700 to 5 mV [Code 12–12–69A]: Current 0.7×10^{-8} amp at 148°C to 3×10^{-11} amp at 59°C.

TABLE 1
Activation Energies for Conduction in Supported Metal Catalysts

Catalyst	Source[a]	Remarks	E, kcal mole^{-1}
Pt–SiO_2 (1%)	A	Unreduced	28.3
Pt–SiO_2 (5%)	B	Reduced	12.0 (2)[b]
Pt–SiO_2 (5%)	A	Unreduced	15.6 (2)
		Reduced	13.2 (3)
Ru–Al_2O_3 (0.5%)	C	Spent	31.2
		Working	19.8 (2)
Pd–SiO_2 (5%)	A	Reduced	11.9 (2)
Rh–SiO_2 (5%)	A	Reduced	14.2
Rh–Al_2O_3 (5%)	D	Unreduced	16.3 (2)
		1st Reduction	20.2
		2nd Reduction	18.4
		3rd Reduction	~8.4 (2)

[a] A, B, D: catalysts prepared in this laboratory; C: Johnson Matthey and Co., pelleted catalyst.
[b] The number in brackets is the number of determinations.

unaltered during the course of a measurement. We attempted to measure the conductivity of the alumina and silica supports, but found it impossible to make electrical contacts with these materials.

The results for catalyst conductivities are summarized in Table 1. Preliminary work showed that the conductivities were ohmic, and that values obtained for E were not dependent on applied voltage.

The features of the results obtained on a set of catalysts, chosen more enthusiastically than wisely, were as follows:

(1) The activation energies are comparable with those found in some catalytic reactions.

(2) It seemed to be possible to distinguish between a spent and a working catalyst (Ru–Al_2O_3, 31.2 and 19.8, respectively). The spent catalyst, no longer active, had been used in many conversions of CO_2 to CH_4.

(3) It seemed that hydrogen reduction lowered the activation energy for conductivity.

After this preliminary study, a second set of experiments was conducted. Here the

TABLE 2
Activation Energies for Conduction in Supported Metal Catalysts

Catalyst	Source[a]	Remarks	E, kcal mole^{-1}
Pt–SiO_2 (5%)	A	Unreduced	41.5 (1)[b]
		1st Reduction	22.4 (4)
		2nd Reduction	25.0 (4)
		3rd Reduction	26.2 (5)
		4th Reduction	24.7 (4)
Pt–SiO_2 (1%)	A	Unreduced	26.0 (3)
		1st Reduction	27.3 (3)
		2nd Reduction	25.5 (2)
		3rd Reduction	20.9 (4)
		4th Reduction	23.1 (2)
Rh–SiO_2 (5%)	A	Unreduced	30.0 (1)
		1st Reduction	24.3 (2)
		2nd Reduction	25.6 (2)

[a] A: catalysts prepared in this laboratory.
[b] Number in brackets is the number of determinations.

object was to find the effect of reduction and catalyst-metal loading on the conductivity. The results are summarized in Table 2.

These show three features.

1. Reduction lowers activation energy.
2. Metal loading makes no significant difference to activation energy for conductivity, once the catalysts have been reduced.
3. Change of metal does not significantly change activation energy, once the catalysts have been reduced.

The effect of moisture was quite noticeable: When it was present, following reductions by hydrogen, a first conductivity run would yield a value of $E = 17.9$ for 5% Pt–SiO$_2$. This value rose to $\sim$24 when the sample was dry.

This pattern of behavior was noted in four out of five possible examples.

The activation energies in Table 2 are all higher by $\sim$10 kcal mole^{-1} than those of Table 1. We think that this is because of much more thorough drying of specimens.

DISCUSSION

The most important feature of the results is that the activation energies are comparable with some found in catalytic reactions. Whether or not there is a direct relationship between E (conductivity) on one of our catalysts and E (catalysis) remains to be established. If reactions on supported catalysts are ionic in nature, then there may well be a relationship.

A major and fundamental question which we have not yet been able to answer is whether the conductivity is electronic, (e$^-$ and p$^+$), or protonic, (H$^+$). Though we have tried it, the Seebeck experiment has not been successful on our powder specimens. It is, therefore, necessary to examine both kinds of conduction process.

Electronic Conductivity

Injection of electrons into vacuum from a cathode has its parallel in injection from a suitable contact into an insulator (*3*). The intersurface energy step ψ may be substantially smaller than the work function φ for metal to vacuum, Fig. 3(a), where $\varphi \sim 4$ eV and $\psi \sim 2$–3 eV. This would mean that catalytic mechanisms would be dependent upon the process shown in Fig. 3(b), and would have activation energies of 40 to 60 kcal mole^{-1}. This is high for most catalytic reactions.

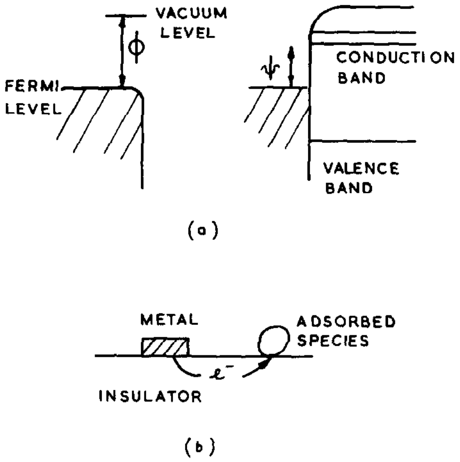

FIG. 3. (a) Schematic energy bands for injecting contact between metal vacuum and metal insulator without traps. (b) Possible electron transport between metal particle and adsorbed species.

Protonic Conductivity

Proton conductivity is a well-established phenomenon. Examples arise in Shakhparonov's dielectric relaxation studies on alcohols and water (*4*), and Maslov and Zotov's approach (*5*) to water as a semiconductor. Thomas *et al.* have made recent studies of proton transport in pyrimidines (*6*) and sugars (*7*). Protons from a Pd electrode can be injected into Li$_2$SO$_4$·H$_2$O to increase its conductivity (*8*), and KH$_2$PO$_4$ is also a protonic semiconductor (*9*). This raises the possibility that the results for supported metal conductivities should be interpreted in terms of protonic conduction. The sensitivity of our system to moisture would support this view.

The catalytic implications, if the catalysts are protonic semiconductors are as follows.

1. Activation energies in catalytic conversions might be a function of water content of reagents and catalysts.

(2) More catalytic systems might be examined as processes dependent on H^+ migration.

This approach to catalytic phenomena may be fruitful. Already the migration of hydrogen from metal to support has been demonstrated by our tracer techniques (*10*), and the phenomenon of spillover has recently been briefly reviewed by Boudart, Vannice, and Benson (*11*).

The development of this work, at present in an early stage, will require the simultaneous measurement of catalytic and conduction activation energies. It will be necessary, perhaps by proton injection, to establish whether or not these systems are protonic semiconductors: in addition the nature of the electrodes and the time effect (*12*) will require careful consideration. We shall also have to examine the possibility that the process may depend on generation of carriers at the electrodes.

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