(^{14}C) TRACER STUDIES OF THE HYDROGENATION OF ACETYLENE OVER SUPPORTED METAL CATALYSTS.

THESIS

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My thanks are also profferred to all colleagues and members of the academic and technical staff who contributed in any way to the work described herein.

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SUMMARY

The adsorption of ethylene, acetylene and carbon monoxide on silica supported rhodium, palladium and iridium, and alumina supported palladium has been studied using a (^{14}C) radiotracer technique. The adsorption isotherms for ethylene and acetylene over each catalyst show two distinct regions; a steep primary region followed by a linear secondary region. In contrast, carbon monoxide adsorption shows only a non-linear primary region, as expected from Langmuir type adsorption. Evidence has been obtained to show that on the primary region acetylene is adsorbed predominantly as a dissociative species of average composition C_2H_a, values of a being 1.4 (Pd), 1.6 (Ir) and 1.8 (Rh); these values being constant throughout the entire primary region. It is also suggested that the primary adsorption of ethylene and acetylene occurs directly on the metal, whereas the secondary adsorption probably involves the formation of overlayers on the primary adsorbed species.

In the adsorption of acetylene at least three types of surface species are recognised; acetylene which participates in the hydrogenation reaction, which is located on the secondary region, acetylene which does not participate directly in the hydrogenation, but which can be removed by prolonged treatment in hydrogen, and acetylene which is permanently retained on the surface at 298K. These latter two species are located on the primary region.

In the hydrogenation of acetylene over each catalyst it has been observed that the activity decreases from reaction to reaction, until eventually a steady limiting activity is attained. On catalysts which had been "run in" to constant activity the adsorption of acetylene and ethylene shows only a limited or no primary region

at all. Although the primary adsorbed acetylenic species do not participate directly in the hydrogenation reaction, the actual rate of hydrogenation is nevertheless directly proportional to the fraction of the primary adsorbed species which can be removed by prolonged treatment in hydrogen. These observations are interpreted in terms of a mechanism for acetylene hydrogenation in which the addition of hydrogen to associatively adsorbed acetylene, located on the secondary region involves hydrogen transfer between a dissociatively adsorbed acetylenic species and the associatively adsorbed acetylene. Direct addition of hydrogen to associatively adsorbed acetylene is not thought to occur.

From studies of the competitive adsorption of ethylene and acetylene, and from the behaviour of added (^{14}C)-ethylene during acetylene hydrogenation, it is concluded that the adsorption of acetylene and ethylene in a catalytically active form occurs on independent sites, located on the secondary region. It has also been observed that during acetylene hydrogenation, a small amount of ethylene hydrogenation occurs independently, this amount varying from metal to metal. The rate of hydrogenation of ethylene in the presence of acetylene is much lower than in the absence of the latter, although the surface coverages of ethylene are independent of the presence or absence of acetylene. This behaviour is interpreted as showing that the hydrogen availability for ethylene hydrogenation is different in the two cases.

With Rh/SiO_2 and Ir/SiO_2 catalysts the hydrogenation of acetylene was poisoned completely by carbon monoxide, while with Pd/SiO_2 carbon monoxide reduce considerably the rate of the hydrogenation reaction.

The poisoning effect of carbon monoxide is interpreted in terms of displacement of adsorbed hydrogen by carbon monoxide.

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CHAPTER ONE

AN INTRODUCTION

General Introduction

Heterogeneous catalysis occurs whenever the rate of a chemical reaction is enhanced by the presence of an interface between two phases. The surface of solids are particularly important as heterogeneous catalysts for reaction between gases or between a gas and a liquid. The problems that have arisen from attempts to use these surfaces to prepare chemicals more speedily and selectively have proved fascinating to chemists and physicists. It is no exaggeration to say that the majority of improvements in utilizing these catalysts for large - scale preparation have come from carefully designed and extensive experiments rather than from the application of chemical theory. For many years, the theoretical treatment of these catalyzed reactions lagged behind the practice, and the practice in turn added little to our theoretical knowledge. The change came with Langmuir's recognition (143) that the intermediates in these reactions are surface compounds formed by the chemisorption of the reactants as ions, radicals or atoms, on the surface of the solid. The precise identification of these intermediates is the key step toward a full understanding of catalysed reactions mechanism. The identification of surface intermediates has proved difficult in all cases, and in many heterogeneous reactions the rate - determining step has not been identified with certainty. Quantitative studies of the extent, rate and energies of the chemisorption of gases have helped and so have measurements of the dipole moment of the adsorbed layer or its electrical conductivity. More recently, infra - red absorption studies have been helpful in identifying the type of bond in adsorbed molecules, while feild emission and electron microscope techniques have helped to locate the adsorbed fragments in relation to the crystal faces and edeges. In the absence of certainty about the mechanisms, it has been impossible to explain in any quantitative manner the catalytic activity of even pure solids, although there are many promising approaches to the problem; it will be some time before the behaviour of the complex surfaces of industrial catalysts is fully understood.

1.1 The Nature of Adsorption:

1.1.1 Physical adsorption:

This usually involves forces of the vander Waals type, similar to those associated with the process of liquefaction. These are weak and of short range, and include "dispersion forces" and short range repulsions. Attractive forces caused by permanent dipoles may also be important in physical adsorption. More than one layer of adsorbed molecules if often formed, depending on temperature and pressure conditions.

Little or no activation energy is involved and the heat of adsorption seldom exceeds 10 kcals/mole. This process is important only at temperatures below the critical temperatures of the gas concerned, usually occuring near the boiling point of the adsorbate at the prevailing pressure.

1.1.2 Chemical adsorption:

This involves forces normally associated with the formation of chemical bonds, either ionic or covalent. Heats of adsorption are, therefore, similar to those encountered in the formation of such bonds and usually lie in the range 10 kcals/mole to 150 kcals/mole. Endothermic chemisorption is, however, sometimes encountered (1). Because of this specific interaction between surface and adsorbate only monolayers are formed. An energy of activation is often involved in chemisorption (2). For this reason and because of the stronger forces involved, this process is important over a wide range of temperature, usually above that at which physical adsorption occurs.

1.1.3 Adsorption isotherms:

That is, plots of quantity of material adsorbed against pressure of adsorbing gas at constant temperature, may be constructed in both cases. The first successful mathematical treatment of adsorption was by Langmuir (3) and it involved a kinetic approach. He considered only monolayer formation on a surface, which was uniform, and on which no interaction between adsorbed molecules occurred. Adsorption was envisaged as a dynamic process with, at any pressure, the rate of arrival of molecules at the surface equal to their rate of departure. The equation so derived, in the case of one adsorbing species, is of the form

$$\theta = \frac{bP}{1+bP} \qquad \ldots . \qquad (1)$$

where θ = the fraction of surface covered,

P = the gas pressure,

and b = a constant.

This simple treatment may be extended to dissociative and competitive adsorption and analogous equations can be derived. The term b in the Langmuir expression is called the adsorption coefficient and is proportional to exp $\left(\frac{-\Delta Ha}{KT}\right)$ where ΔHa is the heat of adsorption of an absorbing molecule. On a uniform surface ΔHa is constant, and thus b is constant. Real systems, however, often display a decrease in ΔHa with increasing surface coverage. Several isotherms have been derived taking such a decrease into account. For example, if the heat of adsorption falls linearly with θ an equation of the form $\theta = A + B \ln p$ may be derived (4). The reasons for the observed decrease in the heat of adsorption with surface coverage have been discussed (5,6). It has been suggested that an inherent surface heterogeneity and as induced heterogeneity, caused by the effect adsorbed material on the work function of the remaining surface, are more important than a dipole - dipole interaction between molecules arriving at the surface and these already adsorbed.

The Langmuir treatment, since it concerns itself with the formation of monolayers, is most frequently used where chemisorption is involved.

Few systems involving physical adsorption obey the Langmuir equation. It has become usual to classify physical adsorption according to five different types, first recognised by Brunauer (7). A successful theoretical treatment of these isotherms was developed by Brunauer, Emmett, and Teller (8) and has come to be known as the B.E.T. theory. This treatment involves the formation of multilayers, the molecules in one layer giving rise to adsorption sites for further layers. An equation of the form

$$\frac{P}{V}\left(\frac{Po - P}{Po}\right) = \frac{P}{Vm} + \frac{Po}{CVm} \quad \ldots\ldots \quad (2)$$

was derived, where:

P = pressure of the vapour concerned,

Po = saturated vapour pressure at the prevailing temperature,

V = volume of vapour adsorbed,

Vm = volume of vapour adsorbed at monolayer coverage, and C = a constant term equal to:

$$(\text{constant}). \quad \exp\left(\frac{E_1 - E_L}{RT}\right)$$

(where E_1 and E_L are the heats of adsorption of the first layer and liquifaction of the vapour respectively).

Equation (2) degenerates to the Langmuir equation where $\frac{P}{Po}$ is low and C is large. These conditions apply in, for example, chemisorption, other equations were also evolved to describe cases where capillary condensation occured.

Both physical and chemical adsorption have been used frequently in determinations of the surface area of substances, especially catalysts. The method based on the B.E.T. equation is useful for the determination of the total surface area. For example, when applied to a supported metal catalyst, it is not possible by this method to distinguish between metal and support. This may be done, however, using a chemisorption method, where the gas used adsorbs specifically on the metal component. Carbon monoxide and hydrogen are among the gases which have been used for this purpose (9,10). Other methods of determining the metal surface area, involving surface reaction, have also been employed (11, 12).

Physical adsorption is normally reversible and the isotherm followed during desorption is usually the reverse of the adsorption isotherm. A hysteresis effect may be observed, however, where the adsorbent is porous, that is, the path followed during desorption is other than that of adsorption. This effect has been reviewed by Everett (13).

Chemisorption on the other hand, which is dependent on the strength of the bonds formed and the nature of the adsorption process, may be reversible, partly reversible, or virtually irreversible.

1.2 Radiochemical Methods.

1.2.1 Mechanistic Work:

Radiotracers have been used in all branches of chemistry in the elucidation of reaction mechanisms, and their use in catalysis is widespread.

The study by Emmett et al. (14) of the mechanism of Fischer - Tropsch synthesis of hydrocarbons is a well documented example of the use of radiotracers. It was shown in this work that surface carbide, formed by the reaction of an iron or cobalt catalyst with ^{14}C -labelled carbon monoxide, played little part in the formation of the products. Using ^{14}C - labelled hydrocarbons, it has also been shown, more recently that the methane yield in this reaction does not arise from hydrocracking of the product hydrocarbons (15).

There are many other examples of the use of radiotracers in mechanistic studies. Hall et al. (16) have studied the kinetics and mechanism of n - butene interconversion over aluminas and silica - alumina, and Ferghan and David (17) have proposed a reaction pathway for the dehydrocyclisation of n - heptane based on the distribution of labelled carbon in the products.

Pines and Goetschel (18) and Tetenyi and Babernics (19) have reported ^{14}C - tracer studies in the liquid phase; the work by the latter authors involved an estimation of the labelled component by isotopic dilution. Based on radiotracer work by Woody et al. (20) and others, the formation of a Y - centre cyclic intermediate has been proposed during the disproportionation of the propenes.

Hughes et al (21) have used ^{14}C - labelled carbon monoxide in a flow system for metal area measurement.

1.2.2. Direct Monitoring and other Adsorption Studies:

The above mechanistic studies have their analogies in other areas of chemistry, but the "direct monitoring" method does not . Here the adsorbed phase is observed directly by a radiation counting device and the amount of radioactive - labelled adsorbate measured. It is made possible by the high sensitivity of radiotracer methods, derived from the case with which single nuclear events may be recorded. The "direct monitoring" method has been used in studies of adsorption at the gas liquid interface usually by use of tritium - labelled compounds. Tajima et al. Seimiya et al. and Jones and Ibbotson have reported work in this field (22 - 27).

Adsorption at solid surface has also been studied by this method. The adsorption of carbon dioxide on nickel single crystals (28) was an early "direct monitoring" study and work on carbon monoxide on the same adsorbent in U.H.V. conditions has also been reported (29).

Lawson (30) has examined the adsorption of formic acid on silver, and Bunrton and Bussiete (31) have described a cell for use at liquid nitrogen temperature for the study of the physiccal adsorption of krypton.

A novel method for the study of adsorption at a glass/solution interface has been described (32). Here a glass scintillator was used both as adsorbent and detecting device.

Like the air/solution interface studies mentioned above this method is limited to the use of isotopes whose emissions are weak.

Thomson and his co-workers have employed radiochemical methods in a number of studies. By direct monitoring of nickel films under conditions where labelled mercury displaced adsorbed tritium it was demonstrated that mercury displacement was never completely efficient; a small percentage of the adsorbed tritium was always retained as single atoms isolated by adsorbed mercury (33). That the hydrogenation of ^{14}C - labelled cratonic and vinylacetic acid on palladium took place on only a few active sites was shown by the use of thiophene as a poison (34). The hydrogenation reaction was seen to be hindered by the presence of thiophene though the adsorption process was not.

The adsorption of gas phase hydrocarbons especially ethylene on transition metal catalysts has been the subject of a number of studes (35 - 43). It has been shown that only a fraction of the surface species formed on exposure of these caralysts to ethylene takes part in subsequent ethylene hydrogenation and that difference metals display different characteristics in this respect.

1.3 The role of Silica and alumina supports:

It has long been known (44) that the activity of metal catalysts is enhanced in metal/support systems compared, with, for example, powder or filament systems, because of the degree of dispersion achieved in supported catalysts. Thus metal - surface to bulk ratios approaching unity can often be attained in these systems. This may be termed a physical effect. However the supposition that this dispersion effect comprises the total role of the support is no longer tenable. It has been demonstrated (45,46) that the same metal can have a specific activity, for the same reaction, which varies widely as the support material used is varied. In the same way the ratio of adsorbed species, where more than one type is observed, may be changed by changing the support.

In the case of ethylene hydrogenation over differently supported platinum catalysts (48), though the same initial rate law was observed and apparent activation energies were all of the same order, different relative rate constants were observed.

In another study of the effect of the carrier material, (49) the amount of metal was held constant while the amount of support was increased. Maxima in catalytic activity were observed and it was suggested that high activity occurred at the metal - support interface.

The exact nature of this metal - support interaction is not well understood, though it has been suggested (45,47) that it is electronic in nature. In this connection Schwab (50), has described how a transfer of electrons from support to catalytic oxide in the oxidation of carbon monoxide on nickel oxide/silver increased the activation energy of the reaction to a marked extent. It is therefore quite likely that, in the reverse case, metal catalyst and semi - conductor oxide support, such an electronic interaction is important. Figueras et. al (51) have pointed out that, in the case of insulator oxides, charge - transfer complexes between metal and support may well provide the mechanism by which support influences the properties of the metal and have demonstrated the activity of such complexes in a platinum/silica - alumina system. Boudart (52) has emphasised the need, where studies of this effect are undertaken, for comparisons between catalysts only be done in terms of catalytic activity <u>per unit surface area</u>, in order that the effect of dispersion may be taken into account. However, where reaction takes place at only a few active sites, as is the case in many systems such as hydrocracking reaction, metal surface area may be a poor guide to the number of active sites, rendering such comparison difficult.

The effect of the support material described above, that is its interaction with the metal component of the catalyst, is but one aspect of its wider chemical role.

Many materials used as carriers have catalytic properties themselves which may be utilised to perform part of the catalytic function. The reforming catalysts used in the petroleum industry are the most important example of this bifunctional catalysis and have been discussed widely (53,54,55).

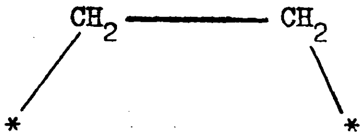
The most frequently invoked mechanism in reforming systems involves hydrogenation - dehydrogenation on the metal component, usually platinum in quantities of less than one per cent by weight, followed by skeletal isomerization and/or craking on the acidic sites of the support. The materials most frequently used as supports are alumina and silica - aluminas.

Reforming catalysts often contain flourine or chlorine in amounts by weight comparible with the metal content. The reaction conditions commonly employed involve temperatures greater than 500°C and high hydrogen partial pressures. Isomerization has also been demonstrated on metal films (56,57) but it seems likely that under reforming conditions the major part of the rearrangement process occurs on the support.

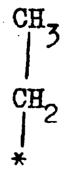
1.4 Ethylene and Acetylene Adsorption on Alumina and Silica:

On aluminas, two types of acetylene adsorption have been reported, a strongly adsorbed species where the acetylene molecule is normal to the surface, and a weakly bonded species in which the molecule lies parallel to the surface (58). In both species the carbon - carbon triple bond is retained. Exchange between the hydrogen atoms of the adsorbate molecules and surface hydroxyl groups has been observed.

No such exchange occurs with adsorbed ethylene on alumina. On some aluminas the adsorbed state of ethylene is the α , β diadsorbed species, E, while on others chemisorbed ethyl groups, F, formed by slow self - hydrogenation are involved (58,59).



E



F

It has been shown that, on alumina, the sites responsible for ethylene adsorption are different from those responsible for the adsorption of acetylene; the two types of sites are probably well separated on the surface (58).

Thermal desorption and deuterium exchange studies (60,61,62) have indicated the presence of weak and strong adsorption sites, the former being mainly responsible for hydrogenation, where an ethylene - hydrogen mixture is present. Where thermal desorption was carried out using an alumina sample which had been exposed to ethylene, the desorbed material consisted solely of ethylene (61).

In a similar way, ethylene itself was the only desorption product, where ethylene had been admitted to a silica sample (63). Acetylene is adsorbed on to silica only weakly, and to a small extent (64). Reid et al. (42,43) by a direct monitoring method found that the adsorption isotherms, of ^{14}C - acetylene and ^{14}C - ethylene on Rh/SiO_2 and Rh/Al_2O_3, occur in two stages; a non-linear primary adsorption isotherm followed by a linear secondary adsorption isotherm, while on SiO_2 and Al_2O_3 the adsorption of ^{14}C - acetylene and ^{14}C - ethylene took place in one linear adsorption process which has a very small gradient in comparison with the gradient of the secondary adsorption on Rh/Al_2O_3 and Rh/SiO_2.

1.5 Surface Migration:

The phenomenon, which has been named "spillover" by Boudart, has been observed by a number of workers, and has been reviewed by Boudart (65). It has been observed, for example, that the reduction of tungstem trioxide was accelerated by the presence of platinum. This was ascribed to a dissociation of hydrogen on the metal, followed by diffusion of hydrogen atoms so formed across the metal/oxide interface. Hydrogen adsorption far in excess of that which could be accounted for by adsorption on the metal component alone was found (66).

The atomic nature of the diffusing species has been supported by E.S.R. studies using a variety of zeolites as catalysts (67). Other examples of "spillover" have been reported (68,69,70).

Sancier (70) has estimated that the distance of migration in the palladium/alumina system was of the order of 0.5 mm.

Sinfelt and Lucchesi (71) have studied the hydrogenation of ethylene on 0.05% Pt/SiO_2, where alumina was added to the catalyst. The rate of hydrogenation was greatly enhanced by the presence of the alumina; the effect was too great for it to be additive. It was concluded that hydrogenation occurred mainly on the alumina, using hydrogen which had been activated on the metal and had migrated to the alumina. In further work using $Pt/Al_2O_3$with which alumina had been mixed, Al_2O_3 (72) it was noticed that the presence of platinum enhanced the removal of adsorbed ethylene from the alumina, on hydrogen admission. This observation was interpreted in terms of hydrogen migration though it was also thought possible that the migrating species was hydrocarbon.

Though the migration of hydrogen from metal to support is well documented, the "spillover" of hydrocarbons has not been observed directly. However such a migration of hydrocarbon from metal to support has been suggested as an explanation for the observation of ethylene and acetylene retained on supported platinum catalysts in for greater quantities than could be explained by hydrocarbon adsorption on the platinum component of the catalyst (39,40). Webb and Macnab, (145), using deuterium and radioactive tracer techniques, show that where as the rates of hydrogenation and 1 - butene exchange, over silica - supported rhodium catalysts, decrease uniformly with increasing mercury coverage, the rate of isomerization is virtually independent of mercury coverage up to $\theta_{Hg} > 80\%$. The results are interpreted in terms of a model in which hydrogenation and olefin exchange occur directly on the metal, while isomerization involves the migration of adsorbed 1 - butene from the metal to the support followed by isomerization on the silica.

Implicit in the generally accepted mechanism of bifunctional catalysis, involving hydrogenation dehydrogenation on the metal and isomerisation etc. on the support, is a migration step between different types of sites. The nature of this migration is not well understood. The use of physical mixtures of metal component and acidic component has let to the suggestion of a gas phase transport of intermediates (73,74,75,76).

Olefins, thought to be the most likely intermediates (74 - 76), have been detected in small quantities in the gas phase (76).

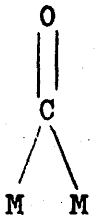
It has also been suggested, however, that in some systems, surface migration may be important (77).

1.6 The Adsorption of carbon monoxide on metals:

The adsorption of carbon monoxide has been very widely studied by almost all of the currently available techniques. Because the adsorption has been assumed to be non - dissociative, and the molecular structure is simple and well understood, CO chemisorption is attractive as a test reaction, where new methods of study are being developed. In addition, its use in metal-area determination has necessitated an understanding of the nature of the adsorption. In particular a good estimate of the ratio of adsorbed molecules to surface metal atoms, is desirable for a large number of metals. The simplicity of the system is, however, deceptive and a degree of uncertainty prevails.

Current knowledge of carbon monoxide adsorption has been reviewed by Ford (78). In early work on the infra - red adsorption by surface species Eischens and Pliskin (79) observed three bands in the carbonyl stretching region. By relating the position of the bands to the spectra of metal carbonyl compounds they ascribed the observed bands to a linear and bridged form of adsorbed carbon monoxide, species G and H.

G



H

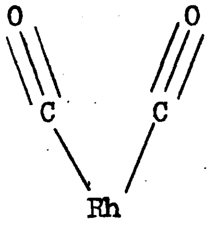
Blyholder (80,81) has, however, offered an alternative interpretation of the observed spectra.

Using a molecular orbital model, he has suggested that all the I.R. obsorption bands may be interpreted in terms of only one structure, the linear form. The low frequency bands assigned by Eischens et. al. to bridged species could occur from linear bonding at edge and corner sites. The first interpretation, however, still finds wide acceptance. Certainly the heterogeneity of the adsorption is not in doubt. Tompkins and his co-workers (82,83) observed a fast rate of adsorption followed by a slower rate, on nickel films. These workers also found that the heat of adsorption on iron remained constant until 30% coverage. Stevens (84) observed a fast removal of carbon monoxide from a palladium surface, followed by a slow removal, on the admission of oxygen. Flash filament desorption studies (78) have also shown that more than one type of adsorbed species or site of adsorption is involved and have favoured an interpretation involving linear and bridged forms of adsorbed species.

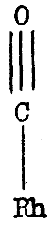
Several studies on single crystal planes have shown that the different forms of adsorption cannot readily be understood in terms of different types of adsorption on different crystal faces. It has been demonstrated that complexities occur even on single planes (85,86,87) Moss et. al. (88,89) have shown that, in the platinum - silica system the relative proportions of the different types of adsorbed species varies with metal concentration and have successfully interpreted their results in terms of bridged species being formed on the crystal faces and linear species at edges and corners.

Rigorous interpretation of infra - red data has been attempted by Bradshaw and Pritchard (90). They observed that on nickel films no bands appeared until the majority of the surface material had been adsorbed; the initially adsorbed species had a very low extinction coefficient.

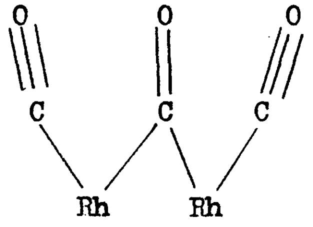
The infra - red results of Yang and Garland (91) revealed three types of adsorption on Rh/Al_2O_3.



I.



G.



J.

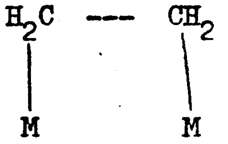
Structure I. was found on an unsintered 2% Rh/Al_2O_3 and, on 8% and 16% catalysts, sintered and unsintered, G. appeared at lower coverages, whilst species I. and J. developed as the coverage increased.

The infra - red results of Palazov (92) revealed that both bridged and linear species exist on 9 % palladium supported on silica catalyst. Evidence is presented that some of the several separate bands seen for bridged species stem from the same species interacting to deffering degrees with neighbouring chemisorbed carbon monoxide. Estimates based on adsorbed amounts suggest that the bridged species has an extinction coefficient which is an order of magnitude greater than that for the firmly bound linear species, but that a loosely bound linear species has an extinction coefficient more comparable to that of the bridged species. A model is suggested for the mode of adsorption that assumes both linear and bridged carbon monoxide bound to the same metal atom. The infra - red results of Guerra and Schulman (93) revealed three types of adsorption on Ir/SiO_2; M - CO, M_2 - CO and M - $(CO)_2$; M - CO being the predominant species.

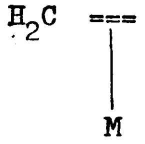
1.7 Adsorbed states of ethylene on metal catalysts:

The adsorption of ethylene, like that of carbon monoxide, has been extensively studied, and the interpretations of the events occurring have often been conflicting.

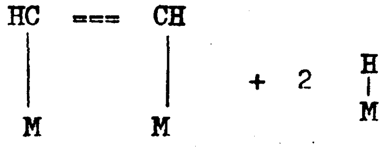
The initial adsorption has been interpreted as either associative, giving structures K or L or dissociative giving, perhaps structure N, or other hydrogen deficient species.



K



L



N

Though Selwood (94) in studies of magnetization changes postulated a mainly associatively adsorbed surface species similar to that proposed by Horiuti and Polanyi (95), dissociative adsorption at room temperature has been more widely accepted.

Self - hydrogenation, resulting in the fast production of gas phase ethane has often been observed (96, 42). Selwood (97) has studied the adsorption of ethylene on nickel/silica over the range of temperature $0^{\circ}C$ to $130^{\circ}C$ and has shown that associative adsorption takes place at low temperature and, as the temperature is raised, dissociation occurs giving rise to self - hydrogenation. Further temperature increase causes carbon - carbon bond rupture and the final formation of surface carbide, the latter as single carbon units. This picture has been qualitatively confirmed by McKee (98). He observed a slow self - hydrogenation at - 78°C, and showed that the extent of dissociation depended on temperature. At 0°C the hydrogen/carbon ratio of the surface species was about 1.5 which fell to 1.0 at room temperature, the latter value being in good agreement with other work (99). It was also concluded that the production of methane, observed as a reaction product, was derived from ethylene not ethane.

Other techniques such as FEM have also indicated that, as the temperature is raised, associative adsorption gives way to dissociation in two steps to a surface carbide, though the latter probably involves two - carbon units (100, 101).

Thus associatively and dissociatively adsorbed species may co - exist on a surface. This conclusion was drawn from a radiochemical study by Cormack et. al. (36). It was shown that on a series of alumina supported catalysts two modes of adsorption occured. One type took part in hydrogenation, molecular exchange with gas phase ethylene and could be removed by evacuation, the other was unaffected by these processes, or at least, could not be removed from the surface by them.

Earlier work (35) on nickel films had shown a similar heterogeneity and it had been suggested that the retained fraction be identified with the hydrogen - deficient species found in other work (99,102).

Further radiochemical studies using a flow technique have again demonstrated the existence of a retained surface fraction for various hydrocarbons, including ethylene, on a variety of catalysts (37,38,39). It was again concluded that this fraction was the residue of dissociative adsorption and self - hydrogenation and it was proposed that the extent of dissociation depended on experimental conditions such as temperature.

In these studies the reactive form has come to be identified with the associatively adsorbed species K or L. This has also been suggested by Bond (103).

McKee and others (98,99) have shown that, on nickel, the hydrogen/carbon ratio is about unity at room temperature. Thus dissociative adsorption gave rise, at this temperature, to two surface hydrogens and a hydrogen deficient species probably with the formula $C_2H_2(a)$.

Beeck (102) assumed this surface complex to have double bond character, structure N, as did Jenkins and Rideal (99).

L.E.E.D. studies on the (111) face of platinum (104) have indicated that the adsorbed species, which result from dissociation, occupy four sites. It is doubtful, however, if, by this technique, one can distinguish between a surface species with double bond character and a species with single bond character (104).

Eischens and Pliskin (105) have pointed out that the surface complex may be fully saturated and have presented infra - red evidence to show that, on nickel - silica, this is probably the case. Infra - red studies of ethylene adsorption have contributed to our understanding of this phenomenon but have also caused some confusion. Most work has been carried out using supported nickel catalysts though supported palladium and platinum have also been used.

Sheppard has stated that infra - red studies may not reveal the presence of reactive intermediates if the appropriate bond intensities are weak (106).

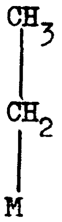
Associatively adsorbed ethylene, corresponding to structure K, has been reported to be present on nickel/silica by some workers (105,107) but not by others (108).

Sheppard (109,110) has reported that this species is present on Ni - SiO_2 only at low temperature, in this work, an n - butyl structure was ascribed to the adsorbed species at room temperature.

Similarly, Peri (108) while observing similar spectra to other workers (105,107) has interpreted them in terms of adsorbed 1 - and 2 - butenes instead of associatively adsorbed species.

Where associatively adsorbed ethylene had been observed, the addition of hydrogen resulted in the formation of adsorbed ethyl groups in one case (105) and in the formation of n - butyl groups in another (107).

Morrow and Sheppard (109,110,111) have studied ethylene adsorption on platinum/silica. They have found the associatively adsorbed species, such as that corresponding to structure N, were also observed. The admission of hydrogen produced ethane in the gas phase and the spectral intensity increased greatly. It was concluded from the latter observation, that initial adsorption had also produced extensively dissociated species, present before hydrogen admission as surface carbide. At higher temperature n - butyl groups appeared and small amounts of n - butane were present in the gas phase. It has been shown, however, (112) that at these temperatures, virtually all of the surface species still retained their C_2 character and that a random high polymer was not formed. Adsorption of ethylene on palladium produced only weak infra - red bands (113); species with double - bond character, structure N, were indicated along with methyl and methylene groups. Admission of hydrogen resulted in a disappearance of the olefinic bonds and an intensification of bonds corresponding to saturated species. This intensification was interpreted as the formation of species corresponding to structure K and structure O:



$$CH_3-CH_2-M$$

(O)

and may have arisen, in part, from hydrogenation of initially present surface carbide.

Surface potential measurements of ethylene chemisorbed on nikel (114) and palladium films (115) are consistent with the π-complex structure L, as originally suggested by Rooney and Webb (144).

Recently, Sheppard and co-workers (116), using an extremely sensitive infra - red interferometry technique, have also obtained evidence for the existence of both a di - σ - bonded and π - bonded species when ethylene is chemisorbed on hydrogen precovered silica - supported palladium and platinum catalysts. These workers alsoclaim that both species are easily hydrogenated, the π - complex being more reactive.

Ethylene polymerisation was reported on supported nickel by Taylor et. al. (117) and subsequently has been noticed many times. Kökes has reported the formation of dimers during ethylene hydrogenation on cobalt (118).

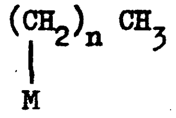
Thermal desorption studies, carried out using silica and alumina supported platinum (40), have also indicated polymerization of ethylene, though it was concluded that this process took place mainly on the support material.

1.8 Adsorbed states of acetylene on metal catalysts:

Eischens and Pliskin (105) reported, from infra - red studies of acetylene adsorbed on supported nickel, evidence for the self hydrogenation of acetylene to ethyl groups (structure O) and the formation of surface carbidic species. These observations were confirmed by Nash and Desieno (119). However, a quite different spectrum was found by Little et. al. (120) - for acetylene adsorbed on palladium, copper and nickel supported on silica glass. Evidence was found for olefinic species. Evacuation did not remove these species but, on the admission of hydrogen, saturated species were formed. On explosively dispersed copper the formation of n - butyl groups and surface carbide has been reported (119), contrary to the olefinic groups observed by Little et. al. (120).

Sheppard and Ward (121) have reported results for acetylene adsorption on silica - supported nickel and platinum using equipment of greater sensitivity and resolution than had been previously possible. On nickel these workers found evidence for an olefinic species, probably corresponding to structure N, though the possibility of the existence of a surface diolefin was not ruled out. A major proportion of the adsorbed material was shown to be in the form of alkyl groups formed by self - hydrogenation and polymerisation. Admission of hydrogen resulted in the formation of n - butyl groups and an intensity increase indicating the initial presence of surface carbide.

On platinum a weak spectrum was observed initially; a large intensity increase was observed on hydrogenation of the surface species. Thus surface carbide formation, accompanied by adsorbed hydrogen formation, took place to a marked extent on this metal. Admission of hydrogen caused the formation of surface - alkyl groups of average structure



$$\underset{M}{\underset{|}{(CH_2)_n}}\ CH_3$$

P.

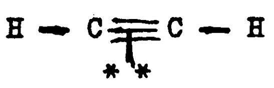
where $n \geqslant 4$. Thus polymers of slightly greater chain length were formed on this metal than on nickel ($n = 3$).

This work, where both olefinic and saturated species were observed on exposure of the catalyst to acetylene, has largely reconciled the observations of previous workers.

Infra - red studies form the bulk of the work carried out on the direct observation of adsorbed acetylene though other techniques have been used. In F.E.M. studies, Hansen et al. (100,101) have reported that, on iridium, the adsorbed state in saturated species involving four carbon - metal bonds, whilst on tungsten, a single dehydrogenation step occurs on heating giving rise to $\underset{**}{C_2}$.

Radiochemical work (38) has shown that the sites responsible for retained species of ethylene and acetylene was shown to adsorb, on a variety of metal catalysts, to almost the same extent on an ethylene precovered surface as on a clean surface.

Both surface potential measurements and observations of the hydrogenation activity of ruthenium and osmium catalysts have suggested (122) that the species active in the hydrogenation reaction is the associatively adsorbed species, structure Q,



$$H - \underset{*\ *}{C \equiv C} - H$$

Q

in which both -bonds interact with surface atoms (144).

Analysis of L.E.E.D. beam intensities for a 2 x 2 chemisorbed layer of acetylene on the Pt (111) surface (123) shows that in the most likely bonding mode the molecule is centred on a triangular site, the carbon atoms are equivalent by symmetry, and relevant C - Pt distances are 2.25 and 2.59 Å. In the other possible bonding mode the molecule is in an approximately twofold position with each carbon coordinating to three platinum atoms, C - Pt distances being 2.47 and 2.65 Å.

1.9 The hydrogenation of acetylene:

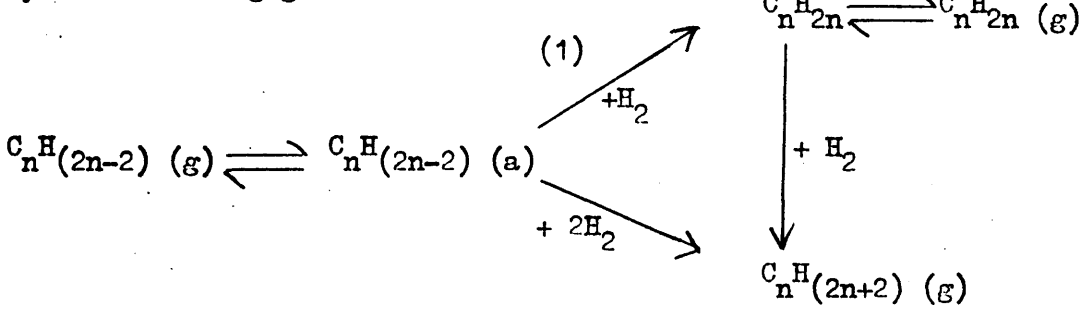
The reaction was first studied by Sheridan and co - workers (124,125,126,127), who investigated the kinetics and product distribution over pumice - supported metals. Subsequently, the reaction has been extensively studied by Bond and co - workers (128,- 134) over pumice - and alumina - supported metals and metal powders. The reaction of acetylene with deuterium has also been investigated over nickel (135,136) and alumina - supported noble group VIII metals (129,137).

For reactions carried out in a constant volume reactor, the shapes of the pressure fall against time curves are dependent upon the initial hydrogen: acetylene ratio, but in general the reaction takes place in two distinct stages. During the first stage the main products is ethylene, with small yields of ethane. The onset of the second stage is generally accompanied by a sharp increase in rate. After the rapid acceleration the main process occuring is the further hydrogenation of ethylene to ethane.

One of the characteristic features of the metal - catalyzed reaction of acetylene with hydrogen is that, in addition to ethylene and ethane, hydrocarbons containing more than two carbon atoms are frequently observed in appreciable yields. The hydropolymerisation of acetylene over nickel - pumice supported catalysts was investigated in some detail by Sheridan (126), who found that between 200 and 250°C, extensive polymerisation to yield C_4 - and C_6 - polymers occured, although small amounts of all polymers up to C_n - , where $n > 31$, were also observed. It was also shown that the polymeric products were aliphatic hydrocarbons, although subsequent studies with nickel - alumina (138) revealed that, whilst the main products were aliphatic hydrocarbons, small amounts of cyclohexene, cyclohexane and aromatic hydrocarbons were also formed. Selectivities defined as $S = PC'_{2}H_{4}/(PC_{2}H_{4} + PC'_{2}H_{6})$ have been observed to decrease with increasing hydrogen pressure and to increase with increasing temperature.

The shapes of the pressure time curves together with the observation that the selectivity remains constant, or nearly so, until the acceleration point is reached has been taken to indicate that the thermodynamic factor is high, that is the presence of acetylene effectively prevents the readsorption of ethylene from the gas phase and also aids the desorption of ethylene. Such a conclusion makes the implicit assumption that the same sites are involved in acetylene and ethylene adsorption.

Different mechanisms have been proposed to explain the hydrogenation of alkynes and olefins. In all these mechanisms there is one assumption regards hydrogenation as hydrogen addition direct to adsorbed unsaturated hydrocarbon or to fragments of adsorbed unsaturated hydrocarbon. The reaction could be represented by the following general reaction scheme:



Thomson and Webb (139) have suggested that this assumption is not valid. From a broad survey of the available literature these authors summarised the basic features of metal catalysed hydrogenation reactions which are not readily explicable in terms of direct hydrogen atom addition to the adsorbed hydrocarbon. The basic features which were considered were as follows:

a. Ethylene hydrogenation belongs to a class of reaction in which the activation energy is found to vary within narrow limits with change in metal.

b. The nature of the metal surface has little effect on catalytic activity in hydrogenation. When films and dispersed supported catalysts were compared on an atom basis rates are virtually equal.

c. When the nature of the reaction is considered in comparison with isomerisation and cracking it is found that hydrogenation is not a structure sensitive reaction.

d. There is at present no satisfactory correlation between the electronic, magnetic or geometrical feature of the catalytically active metals. Thus attempts to correlate activities with work function, holes in the d - band, heats of adsorption, density of electron states etc. have only limited success. The only universal correlation between catalysis and activity is that which involves rates with areas.

Thomson and Webb (139) proposed, as a general mechanism for hydrogenation, a model which unifies all these features of the reaction and which gives an insight into each. They suggest that hydrogenation should be interpreted as hydrogen transfer between an adsorbed hydrocarbon species $M - C_x H_y$ and adsorbed unsaturated hydrocarbon. It should not be regarded as hydrogen addition direct to adsorbed unsaturated hydrocarbon or to fragment of adsorbed unsaturated hydrocarbon.

Their prime aim in making this suggestion is to make the metal only of secondary importance in hydrogenation and to suggest that hydrogenation is but an extension of self - hydrogenation: this latter reaction is self - poisoning but they suggest that the process is continuous in the presence of added hydrogen.

If the features (a - d) are re - examined it can be seen that they all fall into a coherent picture of hydrogenation.

a. Removal of direct dependence on the nature of the metal would account for similarities in the energy barrier to hydrogenation when different metals are used as substrates i.e. rates would depend on hydrogen transfer from M - C_xH_y not from M - H. Variations in frequency factors would arise from different site densities of M - C_xH_y.

b. The form of the metal, film or supported, ceased to be of direct significance if the active center if M - $C_x H_y$.

c. Facile and demanding reactions now appear in a new light. Where a reaction depends for its occurrence on formation of M - $C_x H_y$ then crystallite size and dispersion will not affect the reaction provided equivalent numbers of M - $C_x H_y$ active sites are formed. Catalytic cracking on the other hand will remain as a sensitive reaction in that fission of C - C bonds appears to occur through the formation of M - C bonds to the reacting hydrocarbon.

d. If M - $C_x H_y$ is the active center in hydrogenation then it is not surprising that the correlations sought so assiduously over may years should not exist. It is clear, however, that correlation with area should exist in the sense that increased area will mean increased numbers of active sites. Correlation with physical properties should only exist in so far as they will influence formation and stability of M - C_xH_y centres.

EXPERIMENTAL

CHAPTER TWO

EXPERIMENTAL

2.1 The Reaction System.

2.1.1 The Vacuum System:

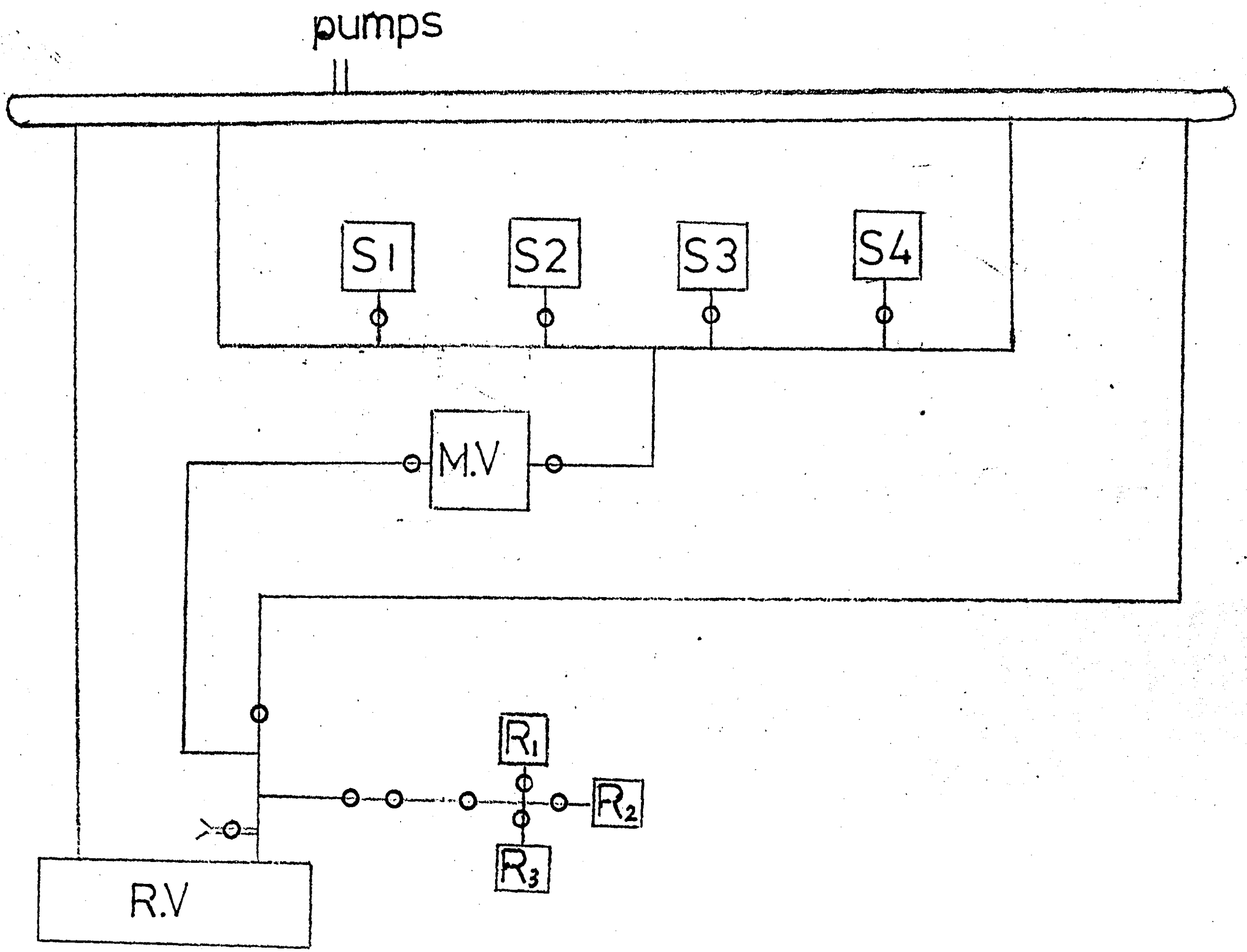
The apparatus consisted of a conventional high vacuum system, and a reaction vessel R.V., maintained at a pressure of 10^{-5} torr or better by a mercury diffusion pump backed by a rotary oil pump.

The vacuum line (figure a) incorporated four one litre gas storage vessels (S_1 - S_4) along with a smaller reservoirs, R_1, R_2, and R_3. These were fitted with three taps in series, the two outer taps being at unequal distances from the middle tap. By using various combinations of the line volumes between these taps, different amounts of the radioactive gas stored in R_1, R_2, and R_3 could be released to the reaction vessel.

The vacuum line incorporated also a mixing vessel M.V., which was used to mix the reacting gases before introducing them to the reaction vessel.

Ampoules of radioactive gas were sealed on to the vacuum line and the breakseals broken by two stainless steel balls manipulated magnetically. Pressures in the vacuum line could be measured in two ways. Over the range 10^{-6} torr to about 0.5 torr the Pirani gauge was used. In the range 1 torr to 1 atmosphere a mercury manometer was used. Pressures in the reaction vessel were measured using a calibrated differential transducer (see section 2.1.3). The reaction vessel (volume 533 cm^3) (fig. b) was similar to that of Reid (42) and involved the use of two intercalibrated Geiger - Muller tubes (Mullard MX 168/01) (see section 2.1.2) which

Fig.a



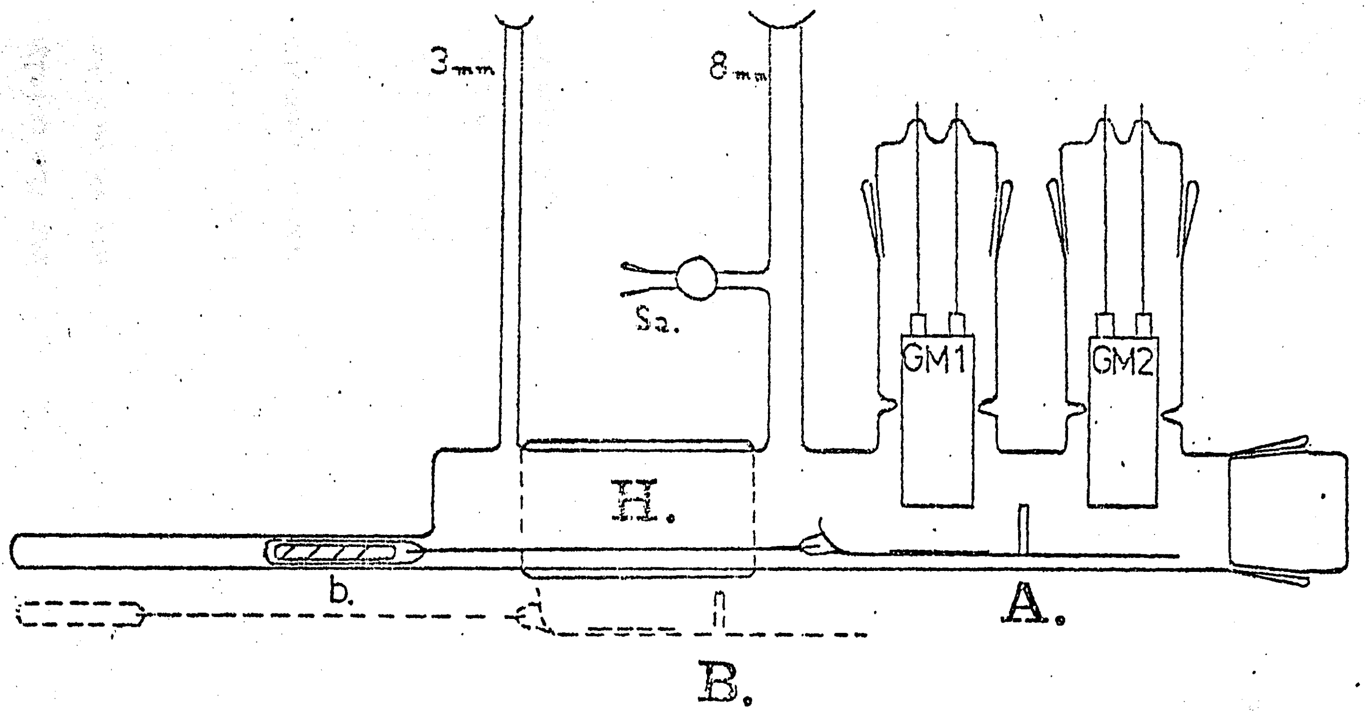


Fig. b The Reaction Vessel

enabled the simultaneous determination of the gas phase and surface without disturbing the catalyst boat. With the boat in position A, Geiger - Muller tube 1, was exposed to the gas phase radioactivity together with the radioactivity from the catalyst surface. Geiger - Muller tube 2 was exposed only to gas phase radioactivity and the empty half of the boat. Thus the amount of radioactive material on the catalyst surface, in equilibrium with the radioactivity labelled gas phase, was obtained by substraction of the count rate recorded by G.M.2 from that recorded by G.M.1.

In order to prevent the radioactivity from the catalyst surface to be detected on G. M. 2., the gas phase counting tube, the obtuse angled emission was eliminated by the inclusion of a thick glass wall (about 3 m m) close to the catalyst area within the catalyst boat itself.

The boat could be moved to position B, inside the reaction vessel heater, H, by use of an external magnet applied to the glass - enclosed metal bar, b, which was attached to the boat by a tungsten rod.

The Geiger - Muller tubes were suspended from tungsten rods sealed through B34 cones and held steady by dimples in the glass walls of the reaction vessel.

The reaction vessel was evacuated either through a 3 m m tap which involved evacuation of the rest of the vacuum line or independently, and quickly, through an 8 m m tap straight to the pumps. The reaction vessel was coupled to a combined gas chromatography - proportinal counter. This permitted the sampling and analysis of the reaction products throughout the course of a reaction (section 2.1.4).

2.1.2 Geiger - Muller Counters:

The Mullard MX 168/01 end - window counters were found to be very satisfactory for this work though their life was shortened by spontaneous collapse of the mica window: this was probably caused by repeated flexing during gas admission and evacuation.

The 'plateau' region was determined for each G. - M. tube by determining count rate against increasing applide voltage. A typical plateau is shown in fig. C.

In order that the gas phase count rate recorded on G. - M.2 could be correlated with the gas - phase count recorded by G. - M.1., the relationship between the two counters had to be determined. This was done, with the empty boat in the counting position, by admitting a small amount of radioactive gas and deriving the correlation factor by relating the count rate of G. - M.2 to that of G.-M.1.

The 'dead time' was set at a constant value by setting the response time of G. - M. pre - amplifier units at 300 μsecs, that is, greater than any likely G. - M. tube 'dead time', an EKCO probe Unit was used together with EKCO scaler.

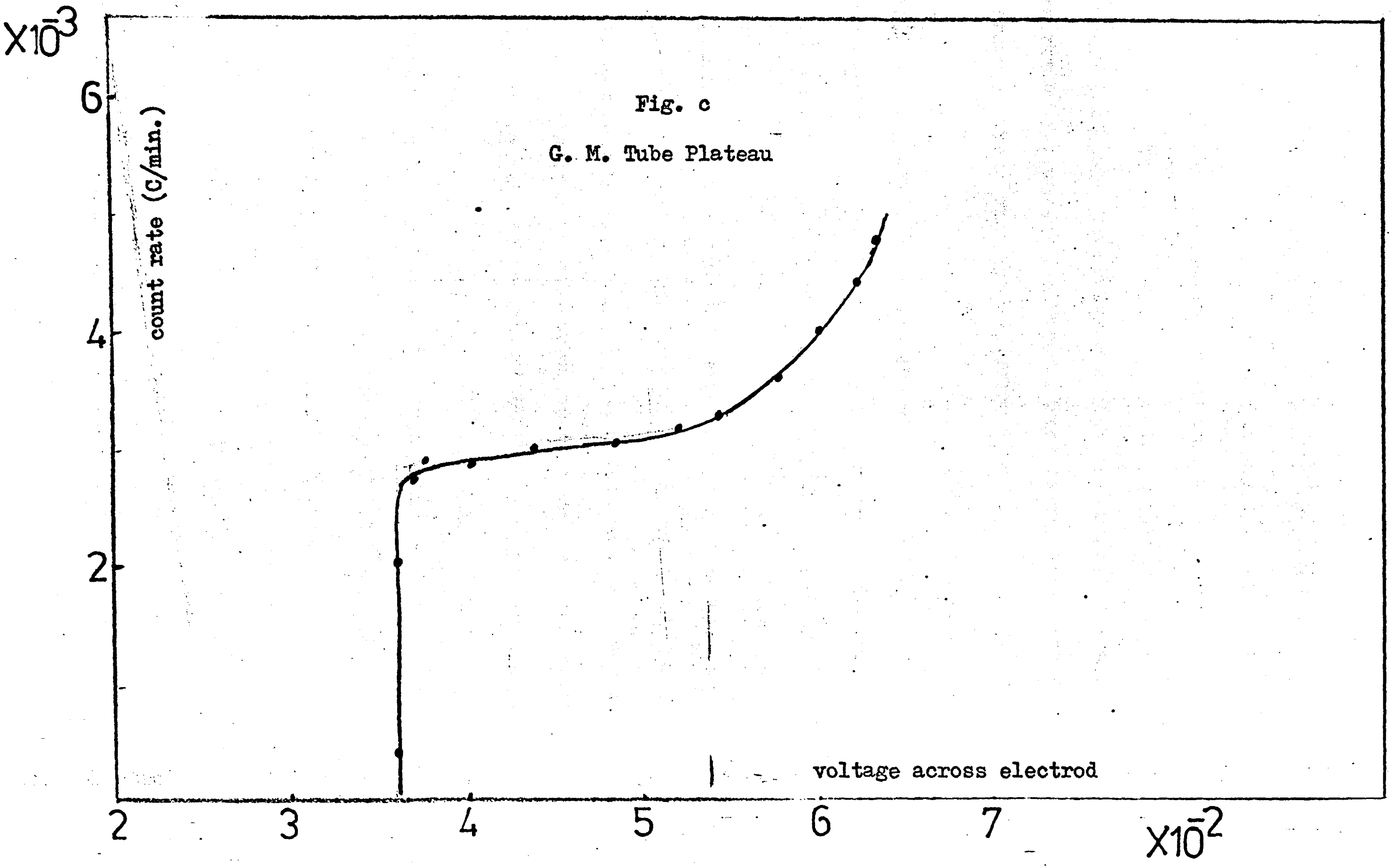


Fig. c

G. M. Tube Plateau

2.1.3 The Pressure Transducer:

Pressure in the reaction vessel was measured by a differential pressure transducer, supplied by Akers Electronic Ltd. comprised a piezo - resistive half bridge element mounted in a substantial brass housing. The silicon beam on which the resistors were mounted was deflected by movement of a pressure sensitive membrane. The transducer was connected to the measuring electronics via a screened multi - core cable.

The input circuitry of the measuring electronics and the transducer formed a Wheatstone bridge configuration. The bridge output was a voltage proportional to the applied pressure differential. Amplification of the signal voltage (of the order of millivolts) was required to provide a meter indication and an output suitable for a pen recorder.

Balance and calibrating controls were provided, the former being used to zero the output for a given reference pressure, the latter being adjusted to give meter scale readings corresponding to pressure units (torr).

The electronic circuit consisted of a differential cross - coupled voltage follower pair feeding a differential amplifier. The voltage follower pair gave a high common - mode rejection and a high input resistance, thus minimising errors in subsequent amplification. The differential gain was set to a nominal value of twelve. The transducer used was of type AE 810 which is suitable for pressure range - 35 to + 35 torr.

The transducer was calibrated against a mercury manometer. The response of the transducer was linear within the pressure ranges used-according to the manufacture's specifications, linearity and hysteresis were within ± 1 %.

2.1.4 The proportional counter:

A proportional flow counter similar to the design of Schmidt, Bleek and Rowland (170) was constructed. The details of the counter are shown in fig. d.

The instrumentation associated with the counter, high voltage supply, pulse amplification and counting, is shown in the general block diagram (fig. e).

The power supply was by a Dynatron (type N 103) unit, the output from which was continuously variable from 300 to 3,300 volts. The amplification was through a Dynatron (type 50 D) pulse amplifier. This consisted of a high gain preamplifier, which was connected to the counter by as short a lead as was convenient (approx. 1 ft.) to minimise interference pick - up, and a main amplifier in which the gain could be altered in 2 db. steps in the range 0 - 40 db. This facility, operated in conjunction with the discriminator bias on the ratemeter and scaler, permitted selection of the optimum conditions to detect pulses of a particular energy. An EKCO N 522 C ratemeter was used. A high speed scaler (EKCO type 530 D), with a dead time of 5μsecs, was connected to the second output of the amplifier. The ratemeter had 100 mv recorder outputs which were connected to a "Servoscribe" potentiometric recorder where the activity in the eluted components was displayed as peaks. From the area of the peaks the total number of counts recorded could be measured. In practice it was more usual to use the recorder trace to determine when to start and stop counting with the scaler.

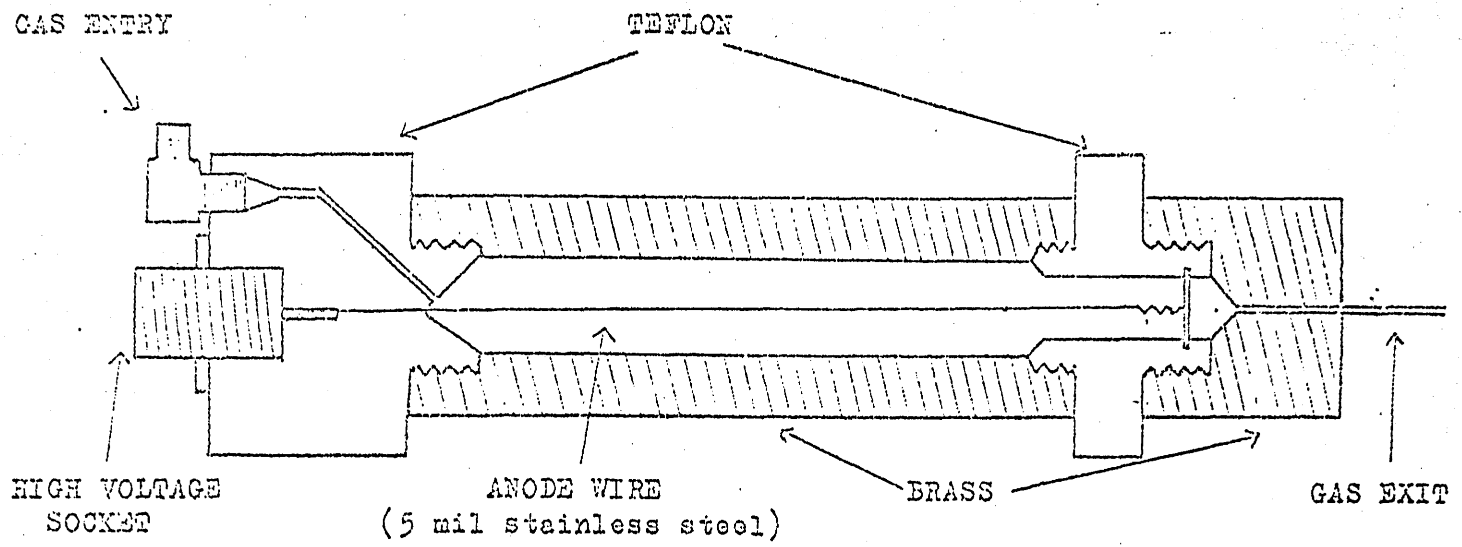


Figure d. The Proportional Counter.

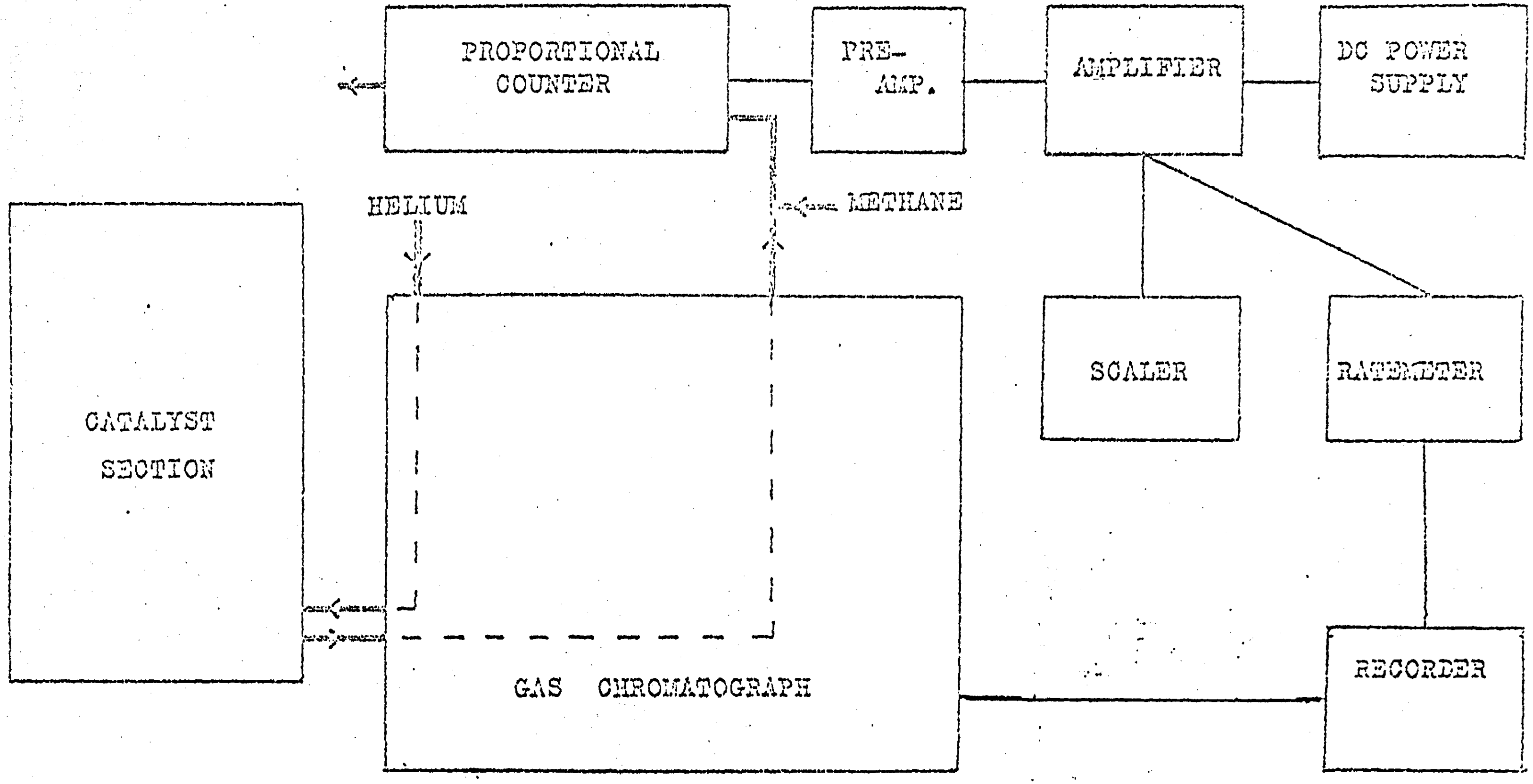

PROPORTIONAL COUNTER
PRE-AMP.
AMPLIFIER
DC POWER SUPPLY
HELIUM
METHANE
SCALER
RATEMETER
CATALYST SECTION
GAS CHROMATOGRAPH
RECORDER

Figure 2.

The performance of the counter, like that of the chromatograph, was dependent upon day to day experimental conditions. Consequently the calibration procedure was a dual process comprising of both an extensive pre - experimental investigation and also a brief check on both counter efficiency and reactant gas activity during each experiment. Although conditions in similar experiments were kept as uniform as possible it was not practicable to reproduce the exact sensitivities in both the chromatograph and counter on every occasion and hence the necessity for regular calibration to be carried out.

In this work, a counting mixture of helium and methane was used and the ratio of helium to methane proved to be a critical factor in the determination of the plateau (141).

A helium flow rate of 60 ml. min^{-1} had to be maintained for chromatographic separations and in a study of the helium/methane ratio, mixture proportions were altered by varying the methane flow rate. It was found that a ratio 10:1 helium to methane gave the best plateau in terms of both length and slope (fig. f). The optimum operating conditions for the proportional counter were as follows:

a	-	Amplifier attenuation	32 db
b	-	Time constant (differentiation)	3.2 μsec.
c	-	Time constant (integration)	1.6 μsec.
d	-	Applied voltage	2.1 KV
e	-	Discriminator bias	15 V.

The quantitative behaviour of the counter was tested by admitting different pressures of C^{14} - ethylene to the chromatography

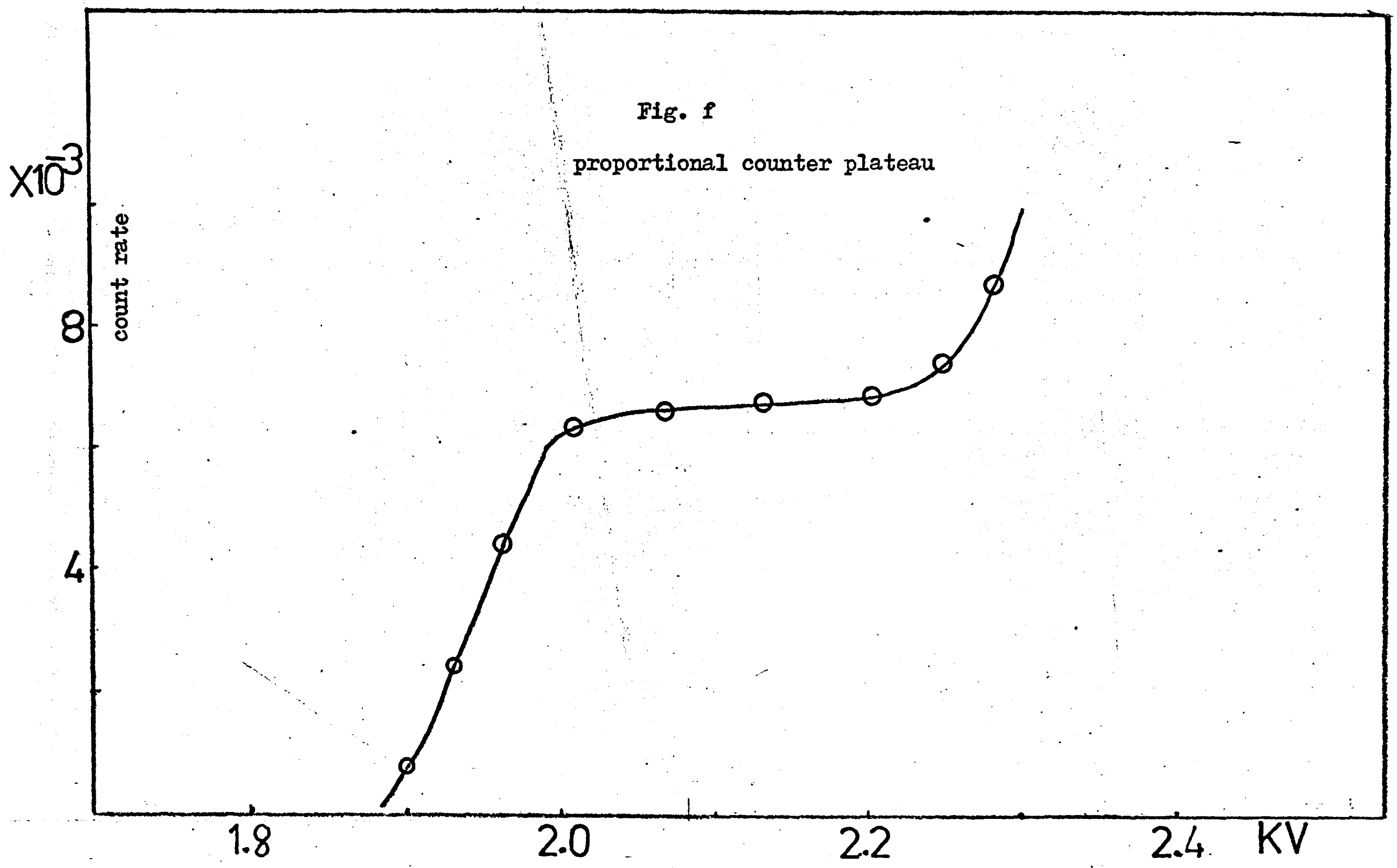
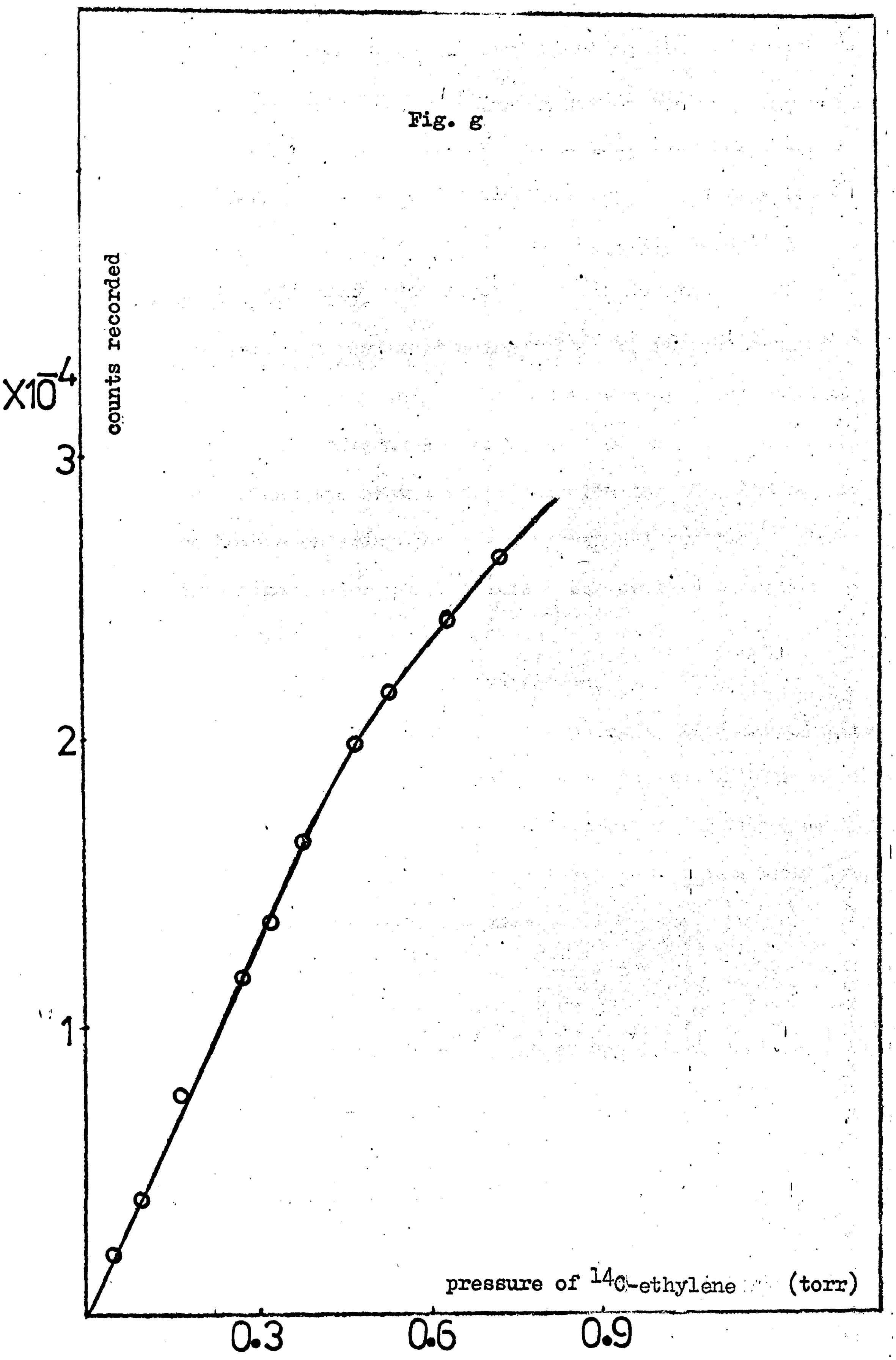


Fig. f

proportional counter plateau

sampling system. This showed (fig. g) that a linear behaviour could be obtained provided the quantity of ^{14}C- ethylene is not too large.

Fig. g


X10^-4
counts recorded
3
2
1
pressure of 14C-ethylene (torr)
0.3
0.6
0.9

2.1.5 The gas chromatography system:

The reaction vessel was connected to a gas sampling sytem (volume 5.5 cm^3), which was then coupled to a combined gas chromatograph - proportional counter. This permitted the sampling and analysis of the reaction products throughout the course of a reaction.

Analysis was performed using a 1 m column packed with 30 - 60 mesh activated silica gel. The column was operated at 80°C with helium as carrier gas at a flow rate of 60 cm^3 min^{-1}. on elution from the column the eluant was mixed with the required amount of methane before entering the gas proportional counter. The output from the katharometer was fed into a Servoscribe potentiometric chart recorder.

A typical trace is shown in fig. h.

The peak area was determined by using a fixed arm planimeter.

In order to eliminate errors due to day to day fluctuations in ambient and instrumental condition, a calibration was incorporated in every experiment. If the experiment was particularly long it was repeated at frequent intervals.

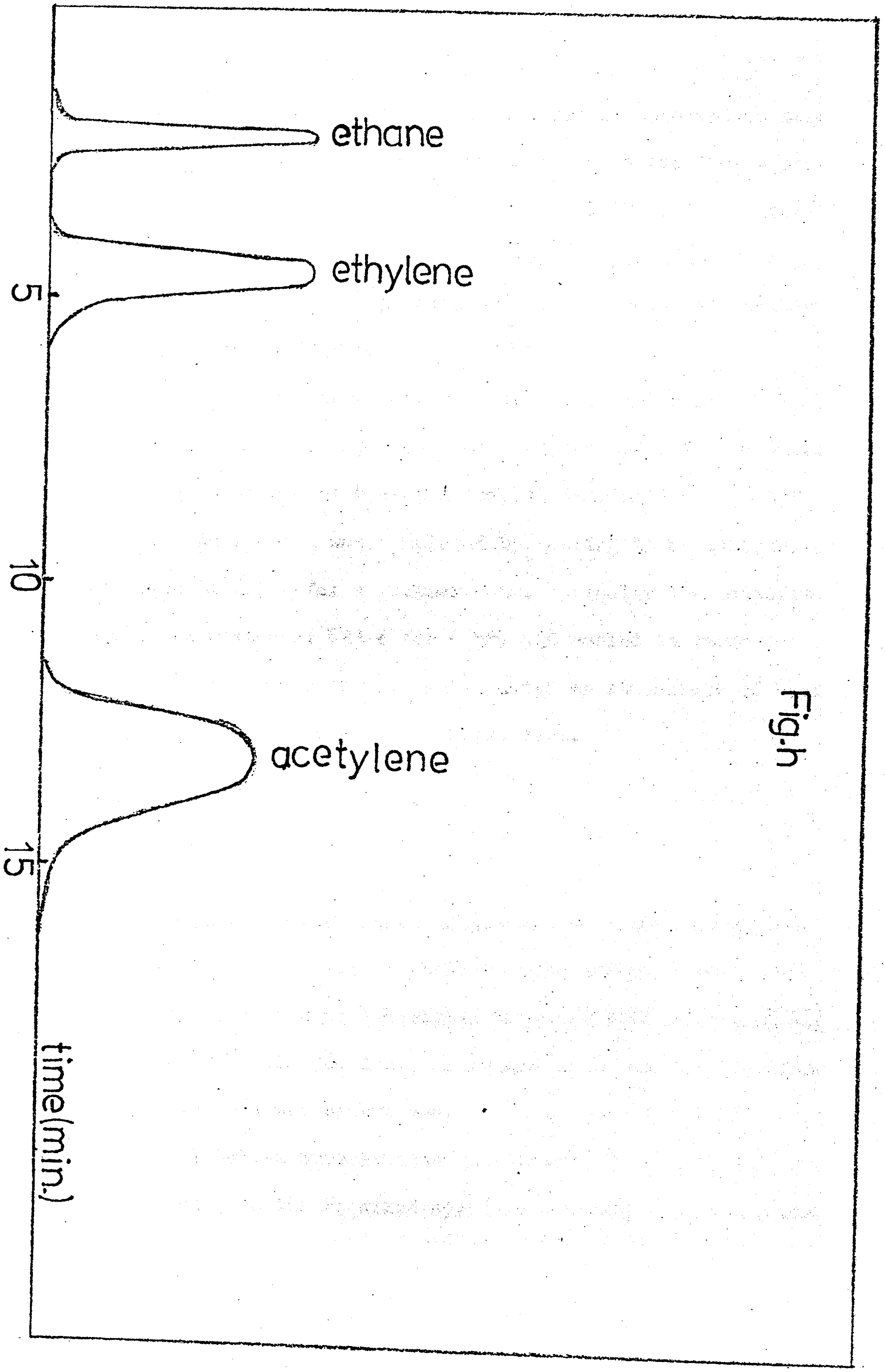


Fig.h

2.2 Catalysts:

The catalysts containing 5 % W/W metal supported on Aerosil silica (Degussa Ltd.) or γ - alumina (Degussa Ltd.) were prepared by adding an agueous solution of the metal chloride, containing the required weight of metal, to an agueous suspension of the support. The excess water was evaporated off and the catalyst finally dried in an air oven at 150°C.

The catalysts were stored as the supported salt until required.

Before use the supported salt was reduced inside the reaction vessel in a stream of hydrogen (ca. 10 cm^3min^{-1}) at 473 K for 12 hr. Activation was completed by heating in an atmosphere of hydrogen at 623 K for a further 6 hr. Finally the catalyst was either evacuated at 623 K for 6 hr. and cooled in vacuo to ambient temperature or was cooled under an atmosphere of hydrogen to ambient temperature before evacuation.

2.3 Materials:

Acetylene (B.O.C. Ltd.) contained both acetone and air. These were removed by a series of bulb to bulb distillations; the purified acetylene contained no impurities detectable by gas chromatography. Ethylene (Matheson Co. Inc.) contained no detectable impurities and was merely degassed before use.

^{14}C labelled hydrocarbons (Radiochemical Centre, Amersham) were diluted to the required specific activity with the purified nonactive hydrocarbon before use.

^{14}C - carbon monoxide was prepared by the reduction of

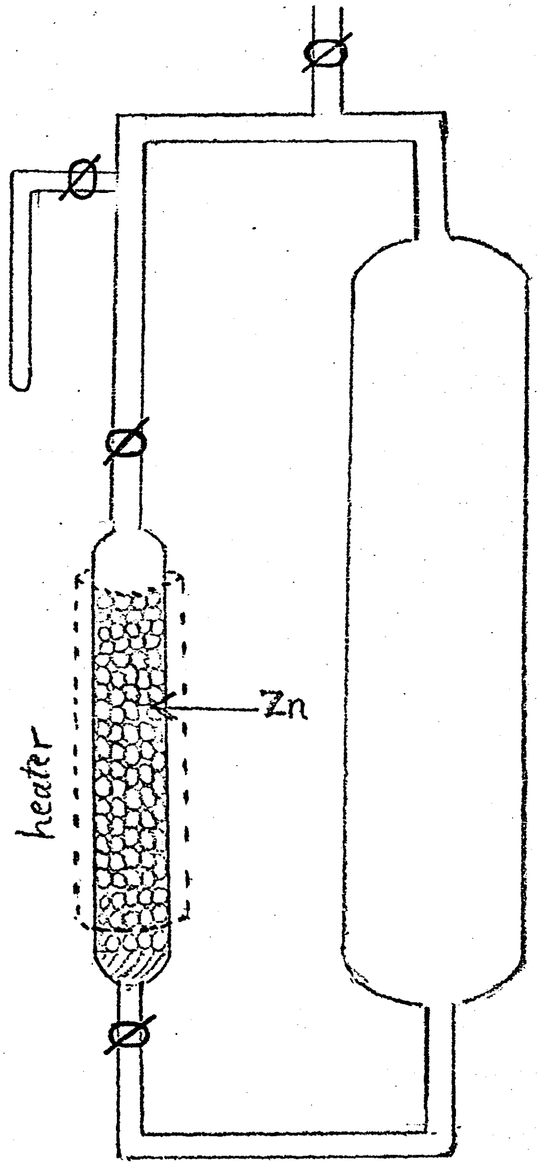
^{14}C - carbon dioxide (Radiochemical Centre, Amersham) with metallic zinc (142).

The apparatus used is shown in fig. i. It consist of a storage vessel and a converter which is a 15 - cm. length of pyrex tubing **25 mm** in diameter.

A thermocouple was attached to the outside wall, and the converter was then placed in a furnace. 50 grams of zinc pellets (about **6 mm** in diameter) were made from a moistened mixture containing 95 per cent by weight zinc dust and 5 per cent Aerosil silica. The silica was used in order to give great porosity and to prevent calogging. The zinc pellets were dried at 110°C for 24 hr. before being placed in the converter. 100 % conversion was accomplished by circulating the $^{14}CO_2$ through the converter at 400°C for 24 hr.

Cylinder hydrogen was purified by diffusion through a heated palladium thimble. The purified hydrogen was used to hydrogenate acetylene. Non purified hydrogen direct from the cylinder was used to clean and reduce the catalysts.

Fig.i



2.4 Experimental Procedure:

2.4.1 Determination of the adsorption isotherms:

The adsorption isotherms were built by addition of small batches of radioactive gas to the reaction vessel containing the catalyst. After the addition of each batch the radioactivity in the gas phase and on the catalyst surface were measured by the two Geiger counters inside the reaction vessel. This process was repeated until the required amount of radioactivity was accumulated on the surface of the catalyst.

2.4.2 Hydrogenation reactions:

Gas mixtures were made up by admitting a measued pressure of hydrocarbon (C_2H_2, $^{14}C_2H_4$) to the mixing vessel and condensing it in the cold finger of the mixing vessel. Hydrogen was then admitted to the required pressure and the vessel allowed to warm up to ambient temperature. The mixture was left for at least 20 min. for mixing to be complete.

Reaction were carried out by admitting the required pressure of the reaction mixture to the reaction vessel and measuring the pressure fall on the transducer. At the required pressure fall, the reaction products were extracted into the chromatography sampling system and then injected to the combined gas chromatography - proportinal counter by means of which the identity of the products and the amount of radioactivity in each of them could be determined.

Aims of the present work

The aim of the work described in this thesis was to use the ^{14}C - tracer technique to study the hydrogenation of acetylene catalyzed by supported rhodium, iridium and palladium.

The work includes:

a - The phenomena of self - poisoning.

b - The poisoning by carbon monoxide.

c - The use of "direct monitoring" techniques to study the adsorption of ^{14}C - acetylene, ^{14}C - ethylene and ^{14}CO on supported Rh, Ir and Pd catalysts.

d - The use of ^{14}C - ethylene as tracer in the reaction of acetylene with hydrogen.

The results will be used to give further information about:

1 - The causes of self poisoning and CO poisoning

2 - The number of the active sites.

3 - The chemical nature of the adsorbed species which are catalytically active in acetylene hydrogenation.

4 - The effect of the support.

5 - To test the success of the new theory (139) of the catalytic hydrogenation of olefins by metals.

6 - The mechanism of acetylene hydrogenation.

CHAPTER THREE

RESULTS

3.1 The Phenomena of Self Poisoning.

3.1.1 Deactivation curves.

A mixture of 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel containing a freshly reduced catalyst at room temperature. The progress of the hydrogenation reaction was followed by measuring the fall in total pressure. Figures1 and 4 show some typical pressure fall against time curves, from which it can be seen that, with Rh/SiO_2 (0.25 g) (Fig. 1) and Pd/SiO_2 (0.003 g) (Fig. 4), the reaction proceeded in two distinct stages. During the first stage a mixture of ethylene and small amounts of ethane was produced. The onset of the second stage was accompanied by a sharp increase in rate.

The "acceleration point", denoted as $-\Delta P_a$, is defined as the pressure obtained by extrapolating the first and second stages of the reaction. After the rapid acceleration the main process occuring was the further hydrogenation of ethylene to ethane.

The acceleration occured at a pressure fall ($-\Delta Pa$) of 16.5 ∓ 1 torr with Rh/SiO_2 and 13.2 ∓ 1 torr with Pd/SiO_2. Up to the acceleration point the pressure-time curves were always accurately first order in total pressure (figures 2 and 5). The results obtained using 0.51 g Ir/SiO_2 (Fig. 7) catalysts were closely similar to those obtained with Rh/SiO_2 and Pd/SiO_2 catalysts. As with the other catalysts the pressure-time curves were first order in total pressure (fig. 8), although they did not show any acceleration point, in agreement with previous reports (146).

With all the catalysts (Rh/SiO_2, Pd/SiO_2, and Ir/SiO_2) the rate of reaction decreased with successive reactions until a constant "steady state" activity was eventually attained. The reaction rate did not tend to zero.

Figure 3 shows the variation of the first order rate constant (k min $^{-1}$) with reaction number for (a) a 0.1 g. Rh/SiO_2 catalyst sample and (b) a 0.25 g Rh/SiO_2 sample.

From figure 3 (a) it can be seen that during the deactivation process, the activity could be partially restored by leaving the catalyst in contact with the reaction products for an extended period. However, once the steady state activity had been achieved this effect was no longer apparent. Storage in hydrogen at room temperature had no effect upon the catalytic activity.

Figures 6 and 9 show the variation of the first order rate constant (K min^{-1}) with reaction number for 0.003 g Pd/SiO_2 and 0.51 g Ir/SiO_2 respectively. It was found that the deactivation process was dependant only upon the number of reaction performed on the catalysts.

Storage of the catalyst under hydrogen at the reaction temperature for prolonged periods, and storage of the catalyst under the reaction products for up to 72 hr. had no effect upon either the progress of catalyst deactivation, or the steady state catalytic activity.

It was observed that pretreatment of the freshly prepared catalysts with acetylene (100 torr acetylene for up to 12 hr. at room temperature) produced only very small decrease in the rate constant (k min^{-1}) of the freshly reduced catalysts.

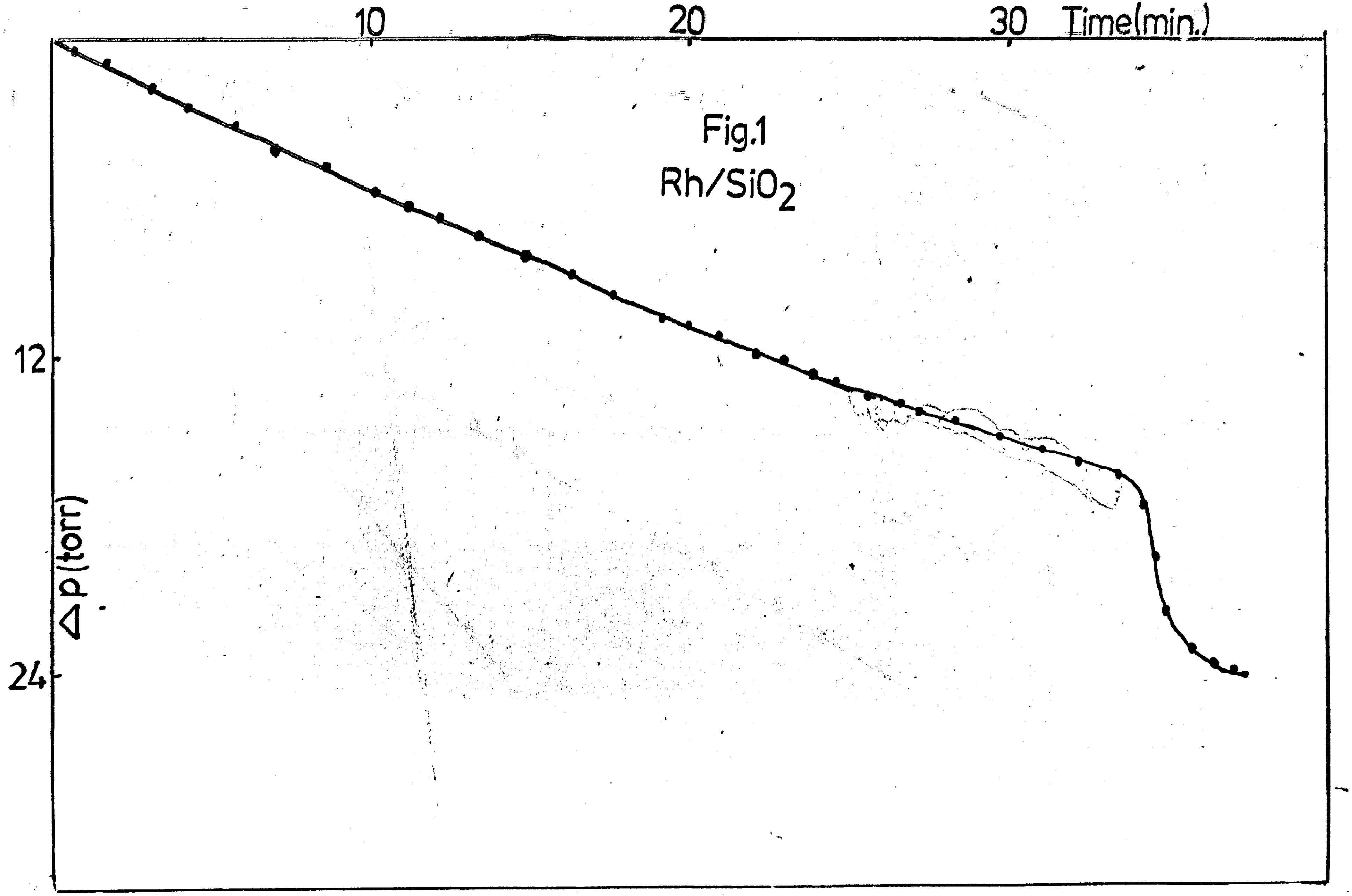


Fig.1

Rh/SiO_2

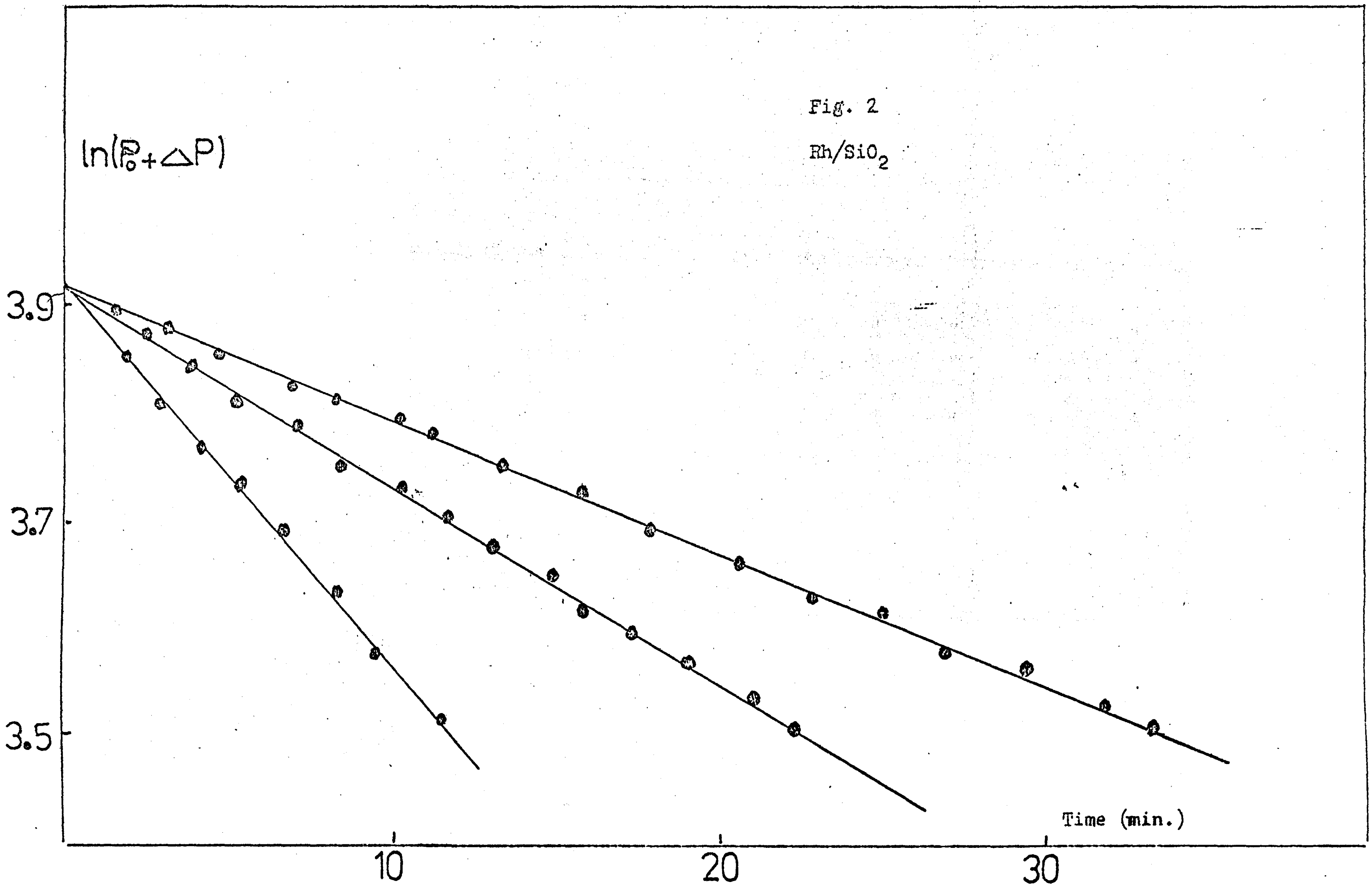


Fig. 2

Rh/SiO$_2$

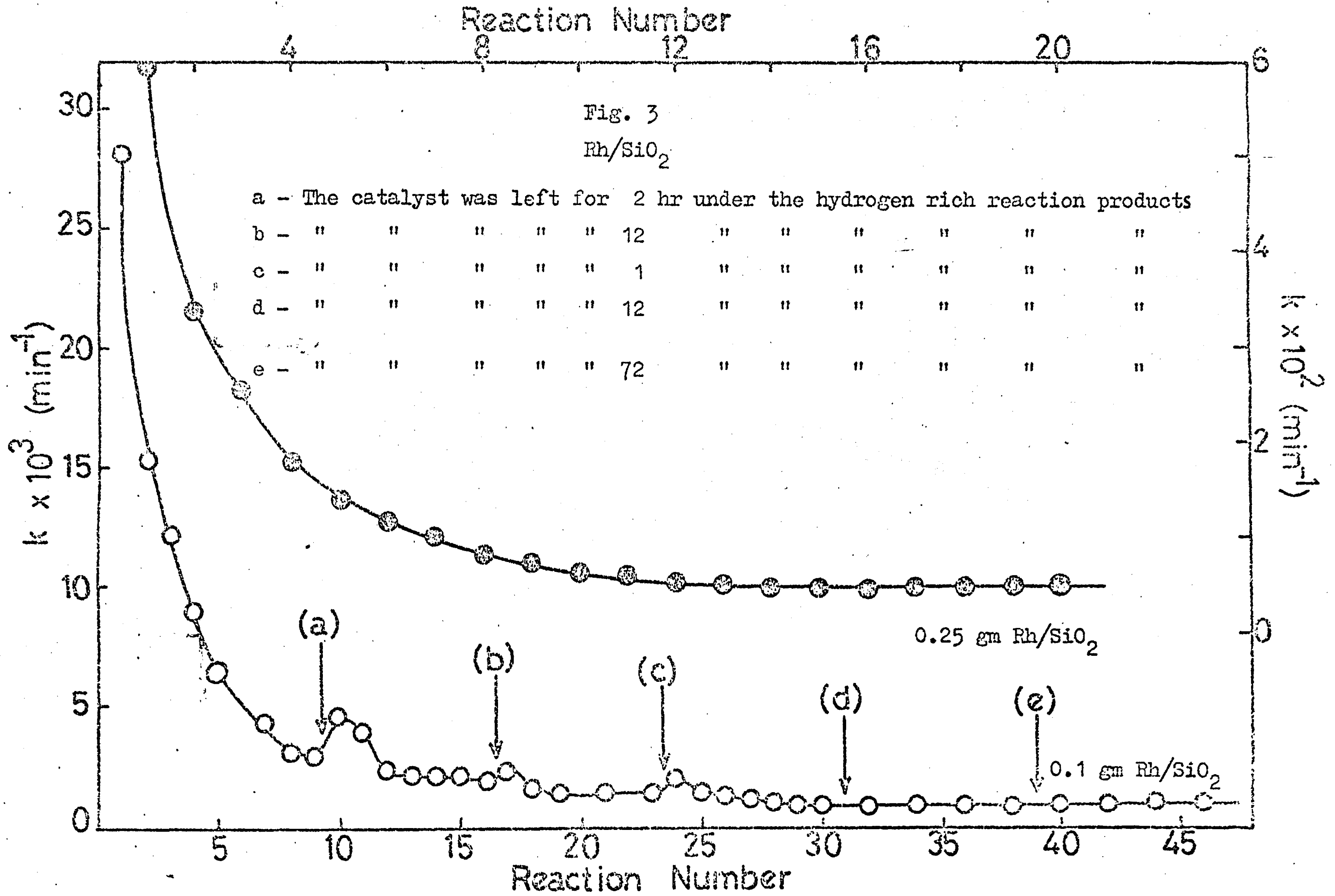
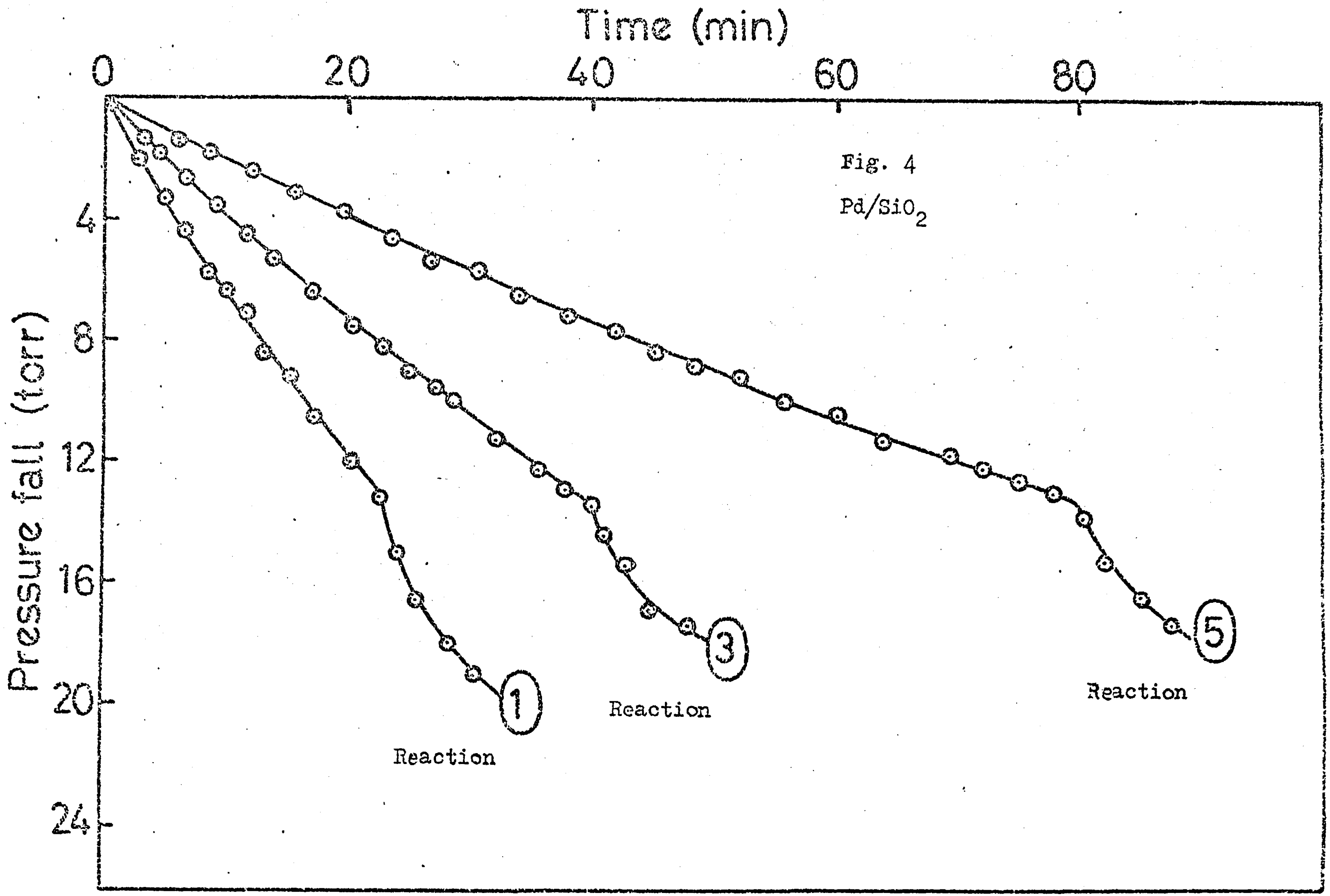


Fig. 3

Rh/SiO$_2$

a – The catalyst was left for 2 hr under the hydrogen rich reaction products
b – " " " " " 12 " " " " " "
c – " " " " " 1 " " " " " "
d – " " " " " 12 " " " " " "
e – " " " " " 72 " " " " " "



Time (min)
0
20
40
60
80
Pressure fall (torr)
4
8
12
16
20
24
1
Reaction
3
Reaction
5
Reaction

Fig. 4
Pd/SiO$_2$

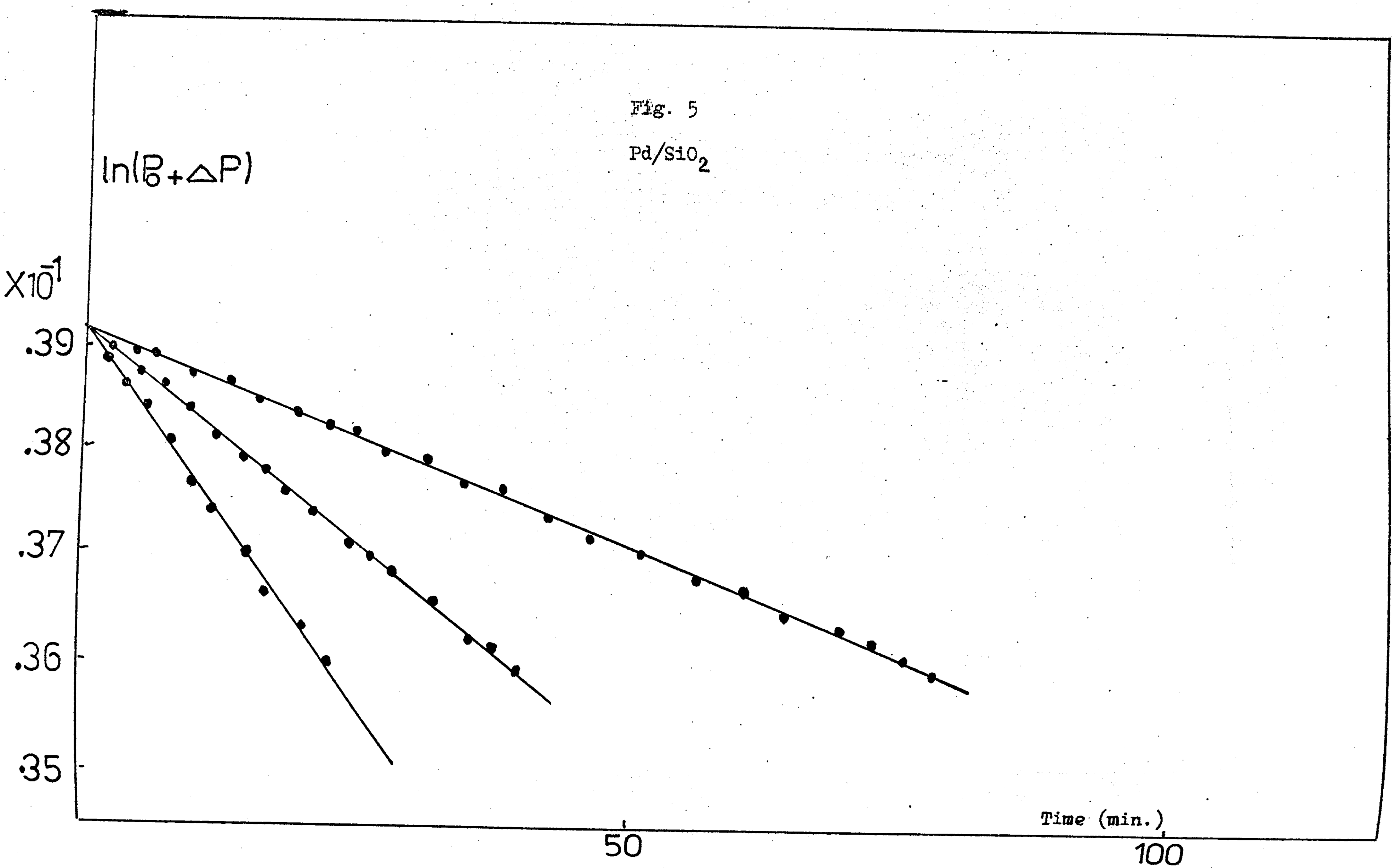


Fig. 5

Pd/SiO$_2$

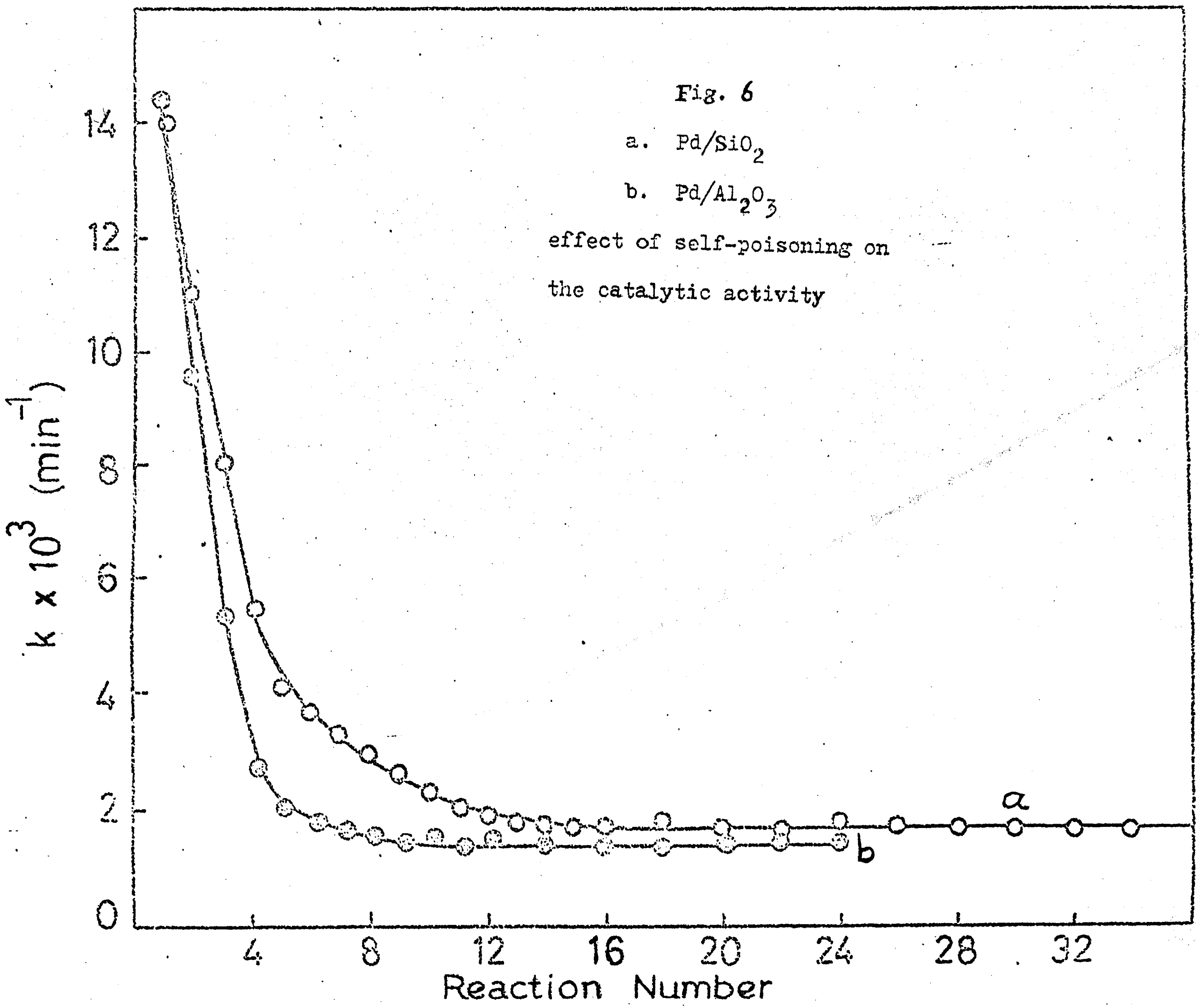


Fig. 6

a. Pd/SiO_2

b. Pd/Al_2O_3

effect of self-poisoning on the catalytic activity

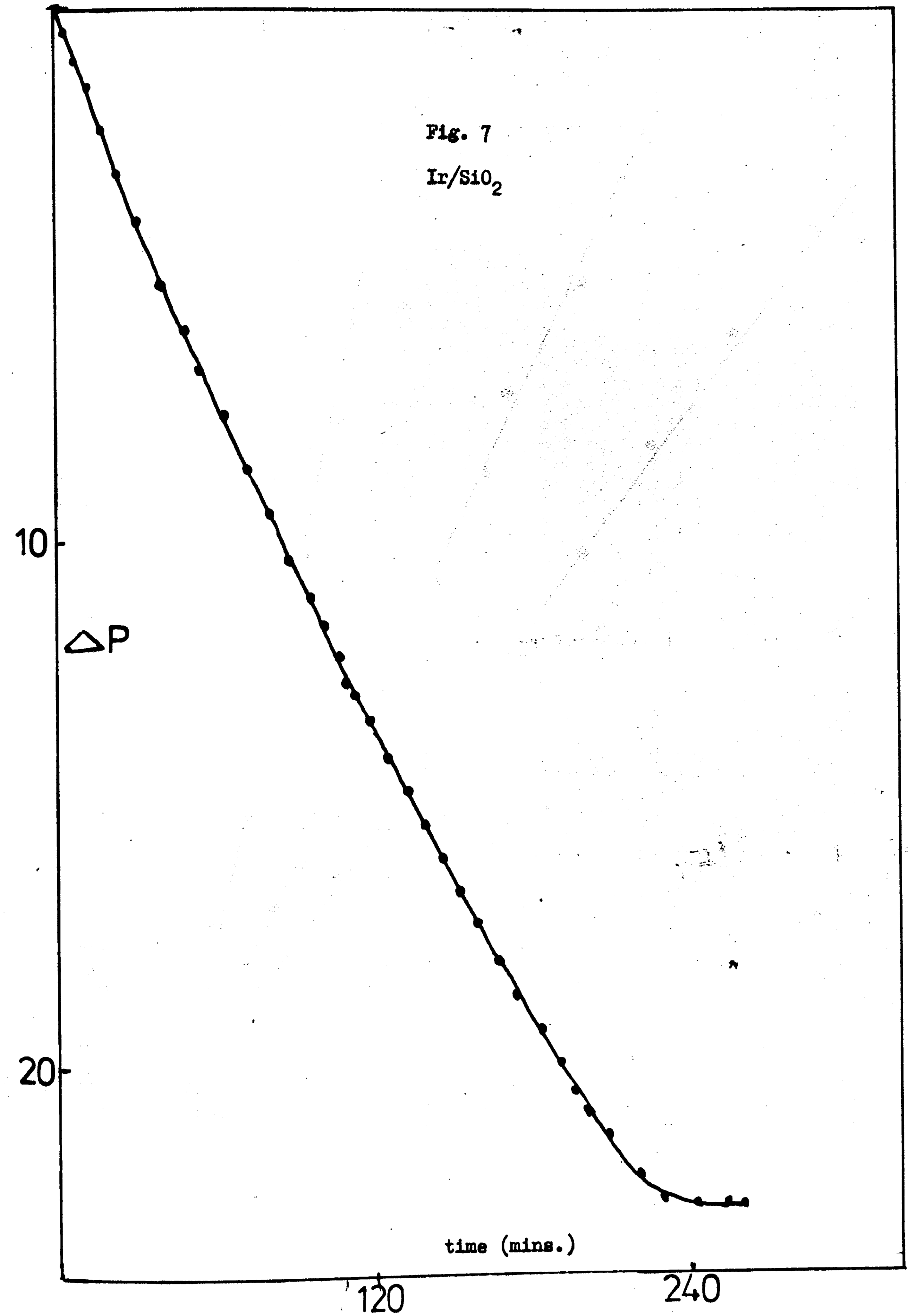


Fig. 7
Ir/SiO$_2$
10
20
ΔP
time (mins.)
120
240

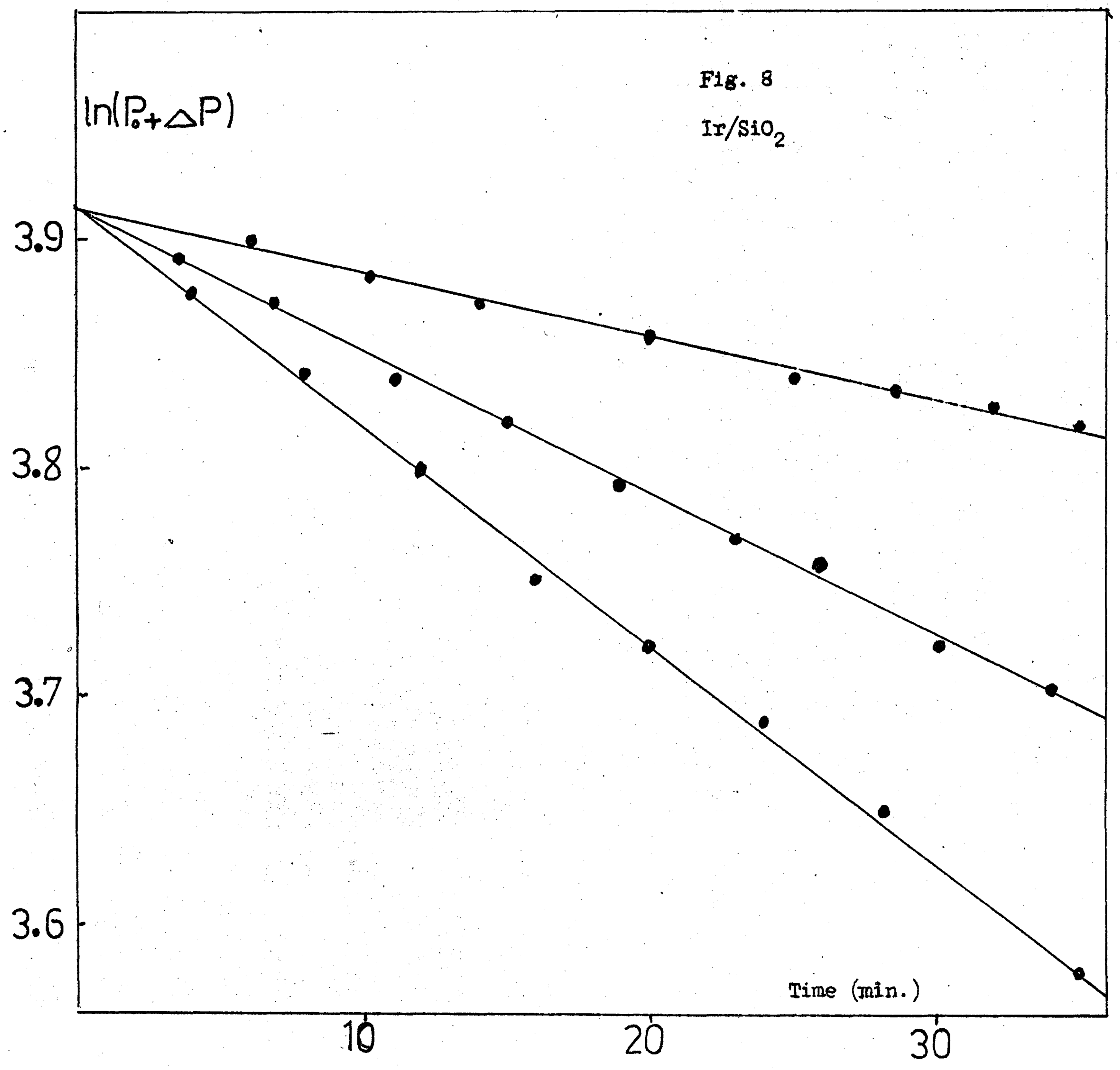


Fig. 8

Ir/SiO_2

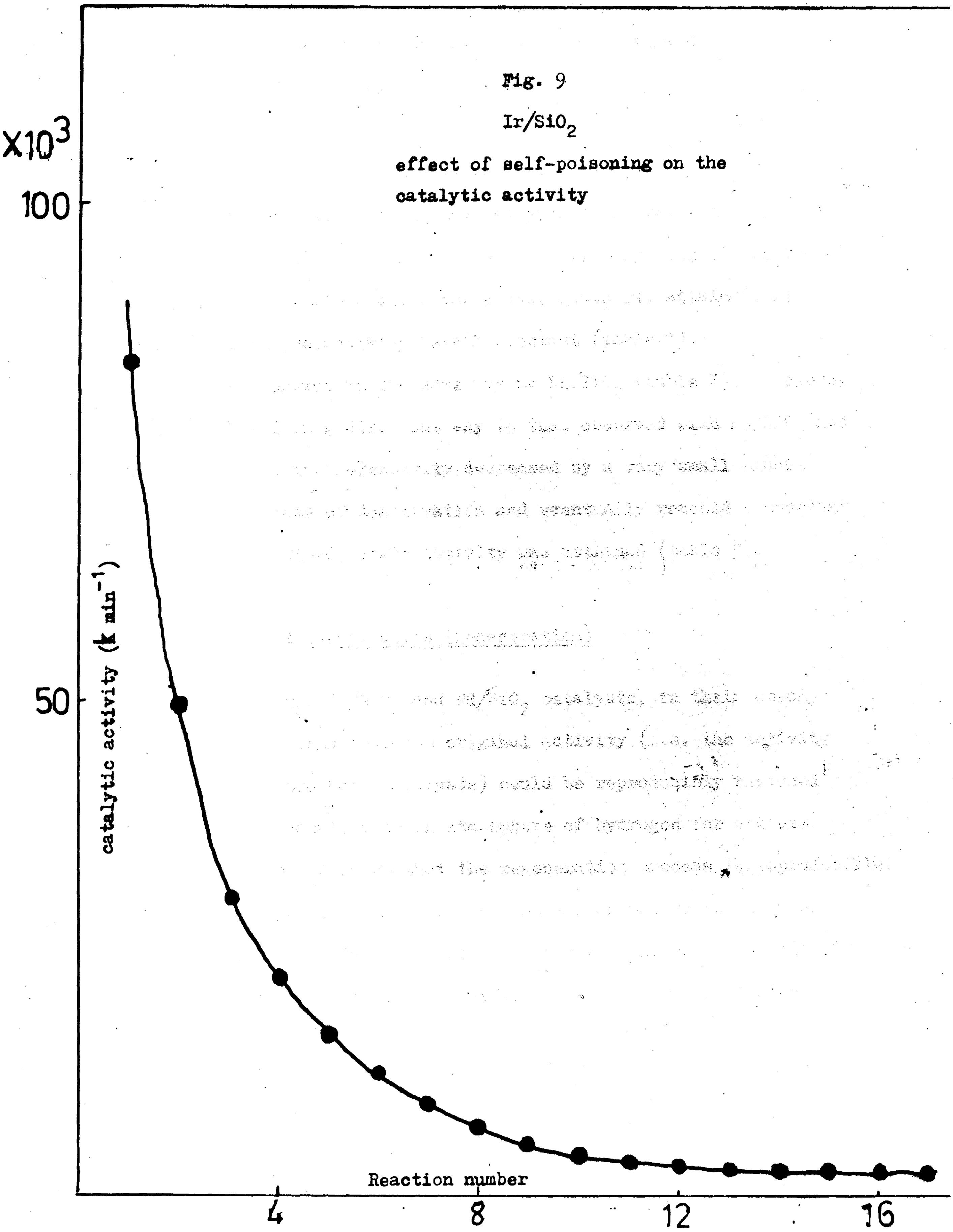


Fig. 9

Ir/SiO_2

effect of self-poisoning on the catalytic activity

3.1.2 Effect of catalytic activity on selectivity.

The change of selectivity ($S = \frac{PC_2H_4}{PC_2H_4+PC_2H_6}$) during the deactivation process was studied by introducing a mixture of 12.5 torr acetylene and 37.5 torr hydrogen to a freshly reduced catalyst (0.1 g Rh/SiO_2, 0.51 g Ir/SiO_2 and 0.003 g Pd/SiO_2). Samples were extracted from the reaction mixture at 40% conversion and analyzed . This procedure was repeated several times during the process of deactivation. It was found that with Rh/SiO_2, the Selectivity very slightly increased during the deactivation until the steady state was attained, at which point the selectivity remain constant (table 1).

Ir/SiO_2 behaved in the same way as Rh/SiO_2 (table 2). However, Pd/SiO_2 behaved in a different way to that observed with Rh/SiO_2 and Ir/SiO_2. Here the selectivity decreased by a very small amount during the process of deactivation and eventually reached a constant value when the steady state activity was attained (table 3).

3.1.3 Catalyst reactivation (regeneration)

With Rh/SiO_2, Ir/SiO_2 and Pd/SiO_2 catalysts, in their steady states, it was found that the original activity (i.e. the activity of the freshly prepared catalysts) could be reproducibly restored by heating the catalyst in an atmosphere of hydrogen for one hr. at 623 K. Table 4 shows that the regeneration process is reproducible. During this regeneration process ethane and methane were produced, although because of the small amounts involved, accurate quantitative analysis of the amounts of each hydrocarbon could not be achieved.

Table 1

0.1 g. Rh/SiO_2

Effect of Self - poisoning on Selectivity

Reaction number	Selectivity
1	0.7204
2	0.7357
3	0.7396
5	0.7468
6	0.7483
7	0.7491
15	0.7518
42	0.7537
44	0.7543
45	0.7529
48	0.7551
49	0.7548
51	0.7541

Table 2

0.51 gm. Ir/SiO$_2$

Effect of Self - poisoning on Selectivity

Reaction number	Selectivity
1	0.1474
2	0,1537
3	0.1573
4	0.1589
5	0.1600
9	0.1624
14	0.1630 (steady state)
15	
16	
17	

Table 3

0.003 gm. Pd/SiO_2

Effect on Self - Poisoning on Selectivity

Reaction number	Selectivity
1	0.9574
4	0.9576
7	0.9568
11	0.9561
16	0.9513
19	0.9435
21	0.9418
25	0.9409
28	0.9402
32	0.9405
33	0.9401

Table 4

Catalyst reactivation

Catalyst	Period of reactivation (hr)	Catalyst reactivity k min^{-1}
0.1 g Rh/SiO_2	12	26.8×10^{-3}
	6	27.1×10^{-3}
	4	26.9×10^{-3}
	4	26.7×10^{-3}
	1	27.1×10^{-3}
	1	27.0×10^{-3}
0.003 g Pd/SiO_2	6	14.0×10^{-3}
	3	14.1×10^{-3}
	1	14.2×10^{-3}
	1	13.8×10^{-3}
0.51 g Ir/SiO_2	6	84.4×10^{-3}
	4	82.9×10^{-3}
	1	83.8×10^{-3}
0.005 g Pd/Al_2O_3	4	14.3×10^{-3}
	2	14.7×10^{-3}
	1	14.5×10^{-3}

3.1.4 Effect of self-poisoning on ^{14}C - acetylene and ^{14}C - ethylene adsorption on Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2:

3.1.4.1 ^{14}C - acetylene adsorption on freshly reduced Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2.

0.2 g Rh/SiO_2, 0.1 g Pd/SiO_2 and 0.51 g Ir/SiO_2 catalysts, after reduction, were evacuated at 623 K for 6 hr. and cooled in vacuo to ambient temperature. The ^{14}C - acetylene adsorptions were examined using ^{14}C - acetylene with specific activity of 0.1 mCi/mM. Figures 10, 15 and 18 show that the adsorption of ^{14}C - acetylene, on Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2, occurs in two distinct regions, a non - linear "primary" region followed by a linear "secondary" region. Similar results have been reported (43) for ^{14}C - acetylene adsorption on supported rhodium catalysts.

The extent of adsorption of acetylene on the secondary region continued to increase linearly with increase in gas pressure; no plateau region was observed although gas pressures in excess of 6 torr were used. In order to test the reproducibility of ^{14}C - acetylene adsorption, it was necessary to find a method whereby all the radioactivity from a previous adsorption could be removed from the surface.

It was found that heating the catalyst in a stream of hydrogen (10-12 ml/min.) at 623 K for 4 hr. removed nearly all of the surface radioactivity. Figures 10, 15 and 18 show that successive adsorptions of ^{14}C - acetylene on the same Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2 catalysts samples were reproducible. Table 5 shows the effect of 37.5 torr H_2 on ^{14}C - acetylene primary region. Catalysts which had been activated, but which had been allowed to cool to ambient temperature in hydrogen before evacuation, rather than evacuated at 623 K for 6 hr., showed similar adsorption isotherms, except that the extent of the primary adsorption was substantially reduced (table 6). Further, with Rh/SiO_2 and Pd/SiO_2 all the adsorbed species on the primary region could be removed by 37.5 torr H_2, while with Ir/SiO_2 only 64% of the adsorbed species on the primary region could be removed by 37.5 torr H_2.

The catalytic activity and the secondary adsorption process were not affected by changing the temperature at which the catalysts were evacuated.

3.1.4.2 Effect of self - poisoning on ^{14}C - acetylene adsorption using Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2 catalysts.

0.25 g Rh/SiO_2, 0.1 g Pd/SiO_2, 0.51 g Ir/SiO_2 catalysts, after reduction, were allowed to cool to ambient temperature in hydrogen before evacuation for 1 hr. The ^{14}C - acetylene adsorption isotherms were built up on the catalysts to an extent such that all of the primary region and a sufficient part of the secondary region were present to enable the "turning points" * of the primary region to be accurately determined. A pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel.

The catalyst activity (the first order rate constant, k min^{-1}) was determined. This process was repeated several times during the process of deactivation. Before each new experiment the catalysts were allowed to stand for 2 - 12 hr. under the hydrogen rich reaction products of the previous experiment to remove the

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* The turning point is defined as the point of intersection between the primary region and the secondary region.

TABLE 5

Extent of Permanent Retention of ^{14}C - acetylene and ^{14}C - ethylene on the Primary Adsorption region at 298K.

Time of treatment in hydrogen = 72 hr.

Catalyst	Adsorbate	Surface Count Rate (min^{-1}) Initial	Surface Count Rate (min^{-1}) Final	% Retention
Rh/SiO_2	^{14}C-acetylene	5696	1821	32
(0.2gm)	^{14}C-ethylene	5223	1729	33
Pd/SiO_2	^{14}C-acetylene	2905	491	17
(0.1gm)	^{14}C-ethylene	853	519	61
Ir/SiO_2	^{14}C-acetylene	8007	3904	49
	^{14}C-ethylene	6706	3375	50

TABLE 6

EXTENT OF PRIMARY ABSORPTION OF ^{14}C – ACETYLENE AND ^{14}C – ETHYLENE ON CATALYSTS EVACUATED AT 623K AND 298K FOLLOWING ACTIVITATION.

ADSORBATE	EVACUATION TEMPERATURE (K)	SURFACE COUNT RATE AT TURNING POINT (MIN $^{-1}$)			
		Rh/SiO_2 (0.2gm)	Ir/SiO_2 (0.51gm)	Pd/SiO_2 (0.1gm)	Pd/Al_2O_3 (0.1gm)
C_2H_2	623	5688	8012	2933	2610
C_2H_2	298	3867	6391	2442	1975
C_2H_4	623	5232	6706	848	500
C_2H_4	298	3497	5331	325	190

adsorbed radioactivity from the catalyst surface.

Figures 11, and 19 show that, with Rh/SiO_2 and Ir/SiO_2, the effect of the deactivation of the catalysts was to reduce the extent of the primary adsorption until it disappears completely as the steady state activity is reached. It can also be seen that the deactivation has no effect on the secondary adsorption process.

Figure 12 and 20 show that, with Rh/SiO_2 and Ir/SiO_2, a straight line was obtained by plotting the turning point of ^{14}C - acetylene primary region against the catalytic activity during the process of self-poisoning.

Figure 16 shows that the effect of the deactivation of Pd/SiO_2 catalyst was to reduce considerably the extent of the primary adsorption without having any observable effect on the secondary region.

3.1.4.3 ^{14}C - ethylene adsorption on freshly reduced Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2.

0.2 g Rh/SiO_2, 0.1 g Pd/SiO_2 and 0.51 g Ir/SiO_2 catalysts, after activation, were evacuated at 623 K for 6 hr. and cooled in vacuo to ambient temperature. The ^{14}C - ethylene adsorptions were measured using ^{14}C - ethylene with specific activity of 0.1 mCi/mM.

Figures 10, 15 and 18 show that the adsorption of ^{14}C - ethylene, on Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2, occurs in two distinct stages, a non - linear "primary" process followed by a linear "secondary" process. Similar results have been reported (42) for ^{14}C - ethylene adsorption on supported rhodium catalysts.

The adsorption of ^{14}C - ethylene on the secondary region continued to increase linearly with increase in gas pressure; no plateau region was observed although gas pressures in excess of 6 torr were used. Table 5 shows the effect of 37.5 torr H_2 on ^{14}C - ethylene primary region.

Figures 10, 15 and 18 also show that successive adsorptions of ^{14}C - ethylene on the same Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2 catalysts samples were reproducible after removing residual radioactivity from previous adsorption. Catalysts which had been activated, but which had been allowed to cool to ambient temperature in hydrogen before evacuation, rather than evacuated at 623 K for 6 hr, showed similar adsorption isotherms to those shown in Figs. 10, 15 and 18, except that the extent of the primary adsorption was substantially reduced (table 6). With Rh/SiO_2 and Pd/SiO_2 all the adsorbed species on the primary region could be removed by treatment with 37.5 torr H_2, while with Ir/SiO_2 only 63% of the adsorbed species on the primary region could be removed by this treatment.

The secondary region was not affected by changing the temperature at which the catalysts were evacuated.

3.1.4.4 Effect of self-poisoning on ^{14}C - ethylene adsorption using Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2 catalysts.

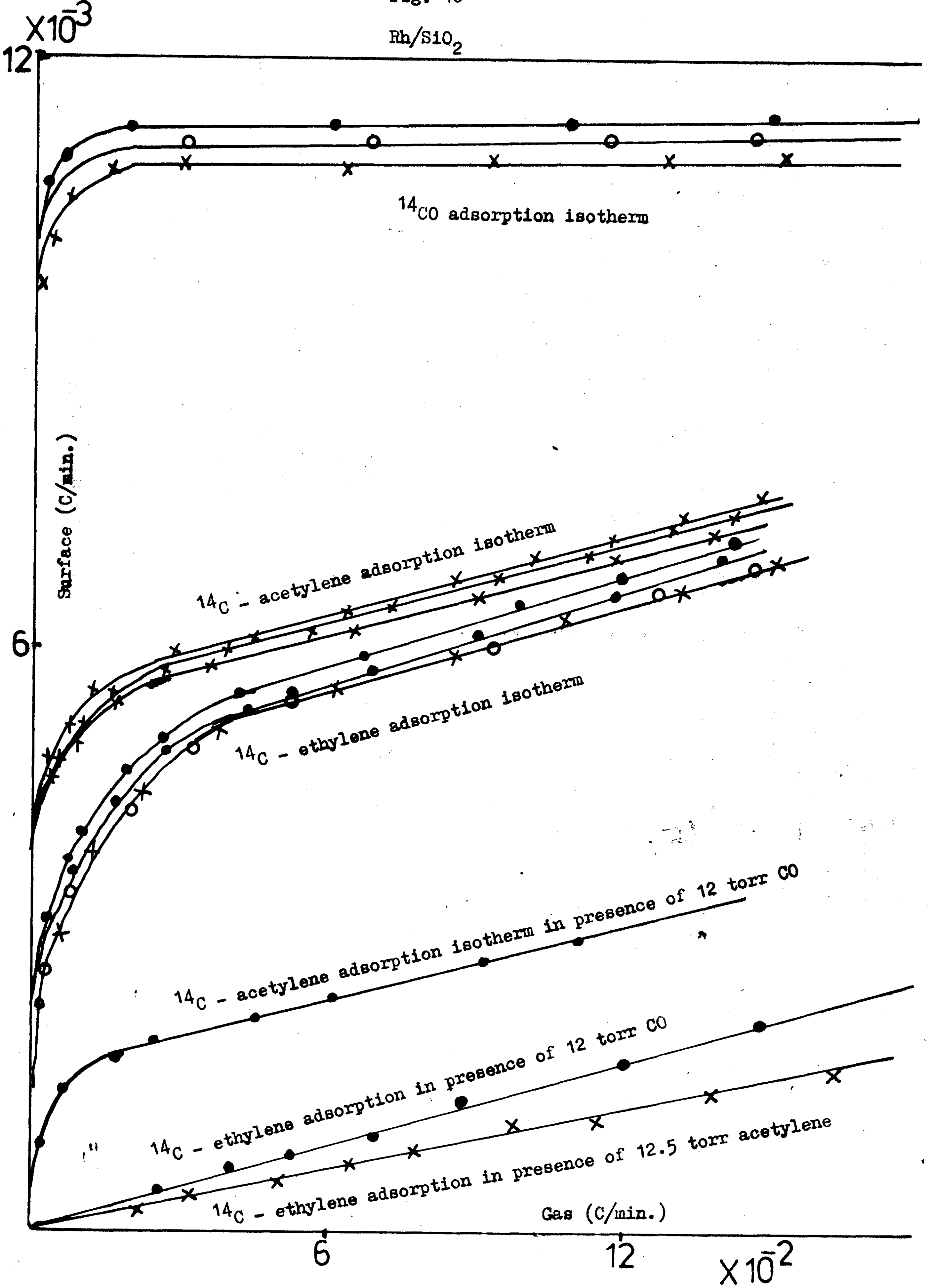
0.25 g Rh/SiO_2, 0.1 g Pd/SiO_2 and 0.51 g Ir/SiO_2 catalysts, after activation, were allowed to cool to ambient temperature in hydrogen before evacuation for 1 hr. The ^{14}C - ethylene adsorption isotherms were built-up on the catalysts to an extent such that all of the primary region and a sufficient part of the secondary region was present to enable the turning points of the primary regions to be accurately determined. A pre-mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel.

The catalyst activity (the first order rate constant, K min^{-1}) was determined. This process was repeated several times during the process of deactivation. Before each new experiment the catalysts were allowed to stand for more than 2 hr. under the hydrogen rich reaction products of the previous experiment to remove the adsorbed radioactivity from the catalyst surface.

Figures 13, 17 and 21 show that, with Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2, the effect of the deactivation of the catalysts was to reduce the extent of the primary adsorption until it disappears completely as the steady state activity is reached. It can also be seen that the deactivation has no effect on the secondary adsorption process.

Figure 14 and 22 show that, with Rh/SiO_2 and Ir/SiO_2, a straight line was obtained by plotting the turning point of ^{14}C - ethylene primary region against the catalytic activity during the process of self-poisoning.

Fig. 10


Rh/SiO$_2$
X10^{-3}
12
6
Surface (C/min.)
^{14}CO adsorption isotherm
^{14}C - acetylene adsorption isotherm
^{14}C - ethylene adsorption isotherm
^{14}C - acetylene adsorption isotherm in presence of 12 torr CO
^{14}C - ethylene adsorption in presence of 12 torr CO
^{14}C - ethylene adsorption in presence of 12.5 torr acetylene
Gas (C/min.)
6
12
X10^{-2}

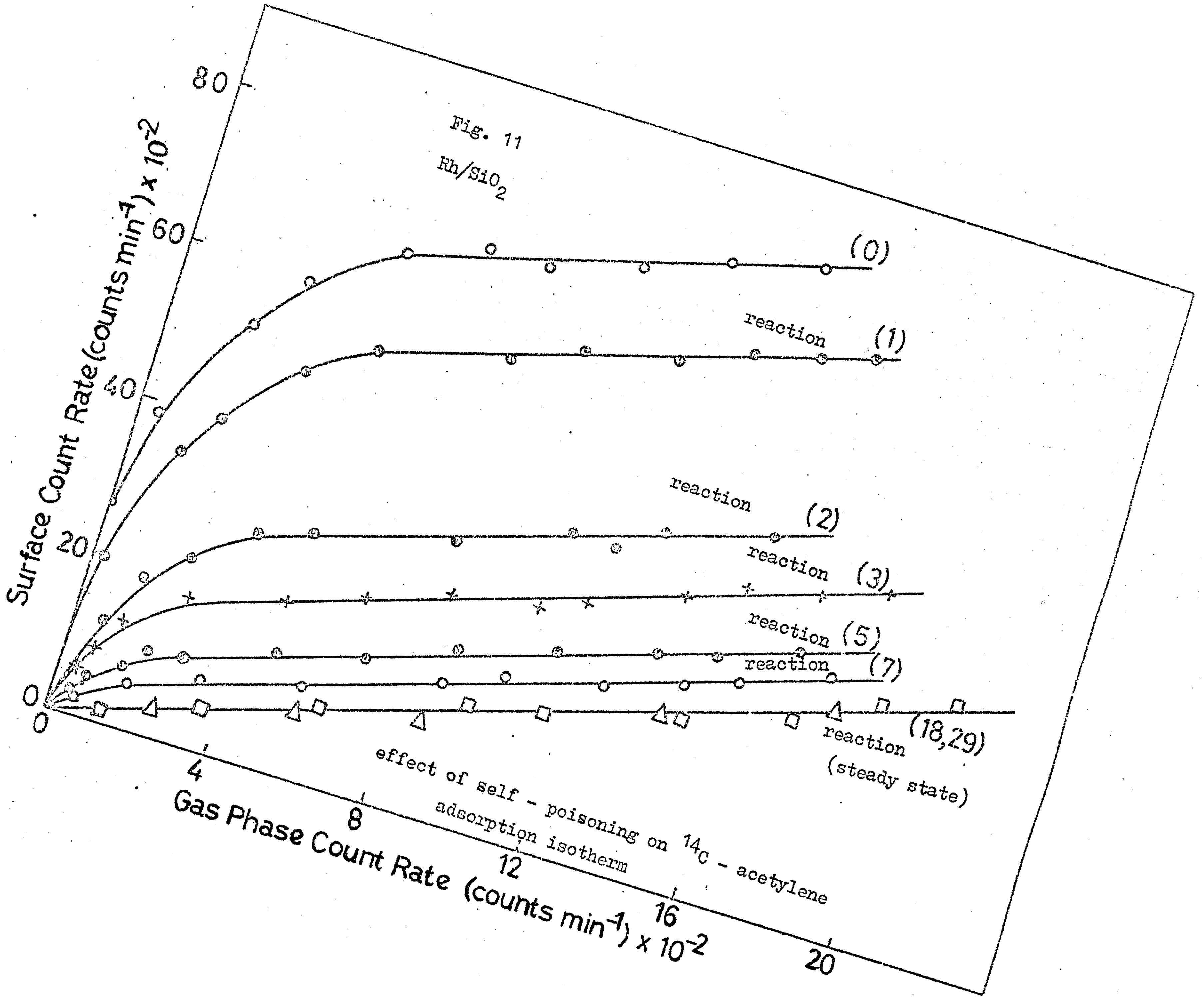


Fig. 11

effect of self - poisoning on ^{14}C - acetylene adsorption isotherm

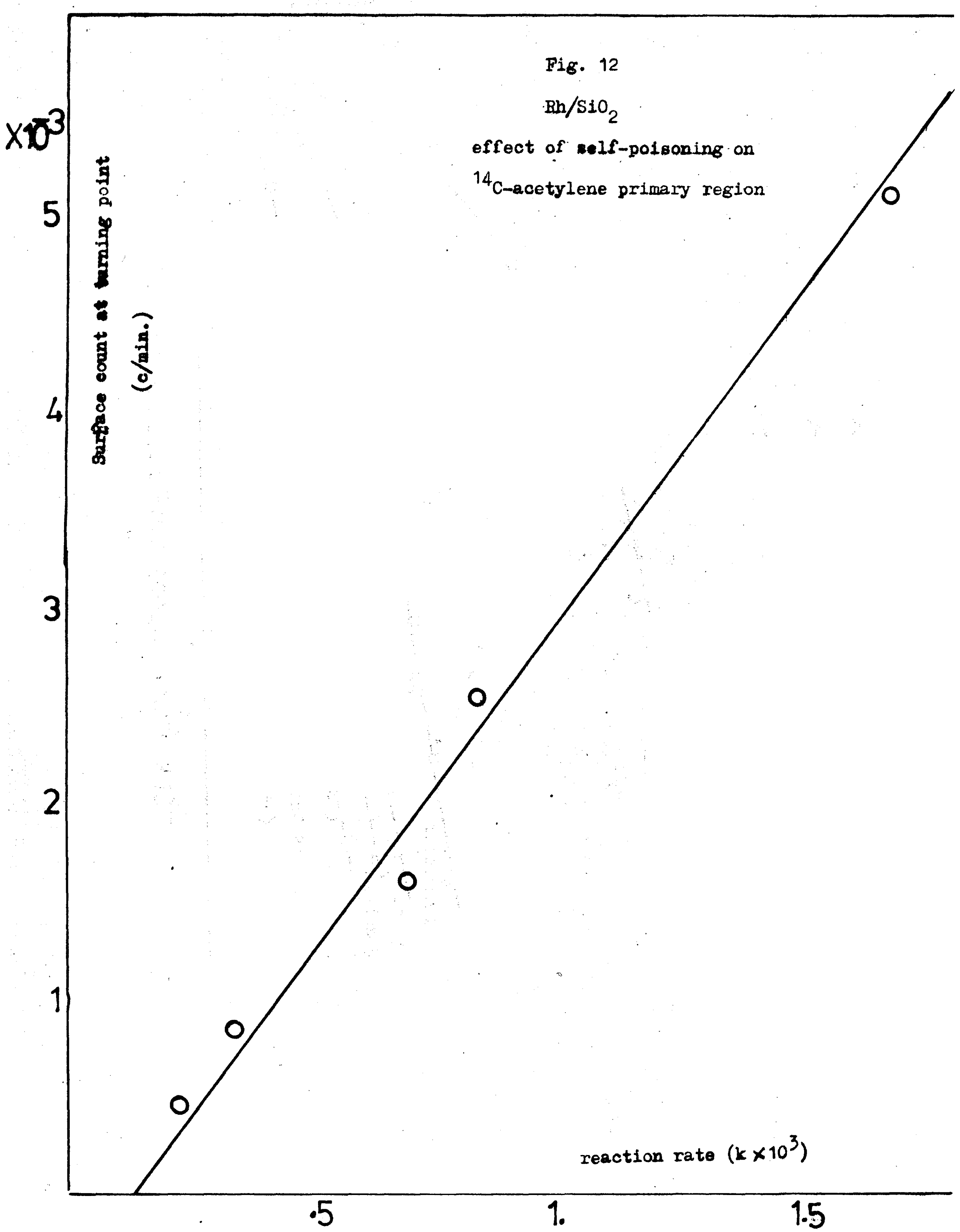


Fig. 12

Rh/SiO_2

effect of self-poisoning on

^{14}C-acetylene primary region

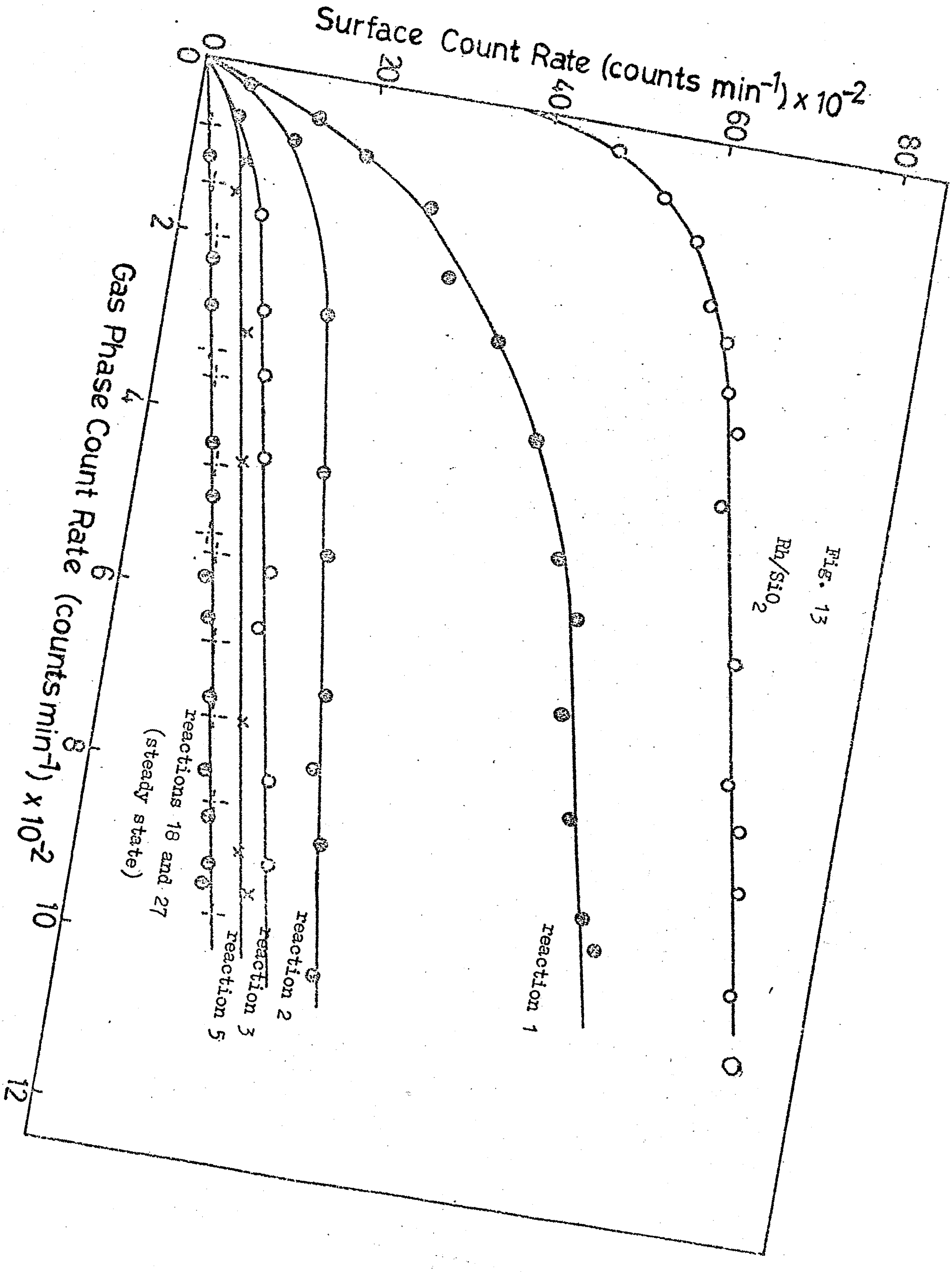


Fig. 13

Rh/SiO$_2$

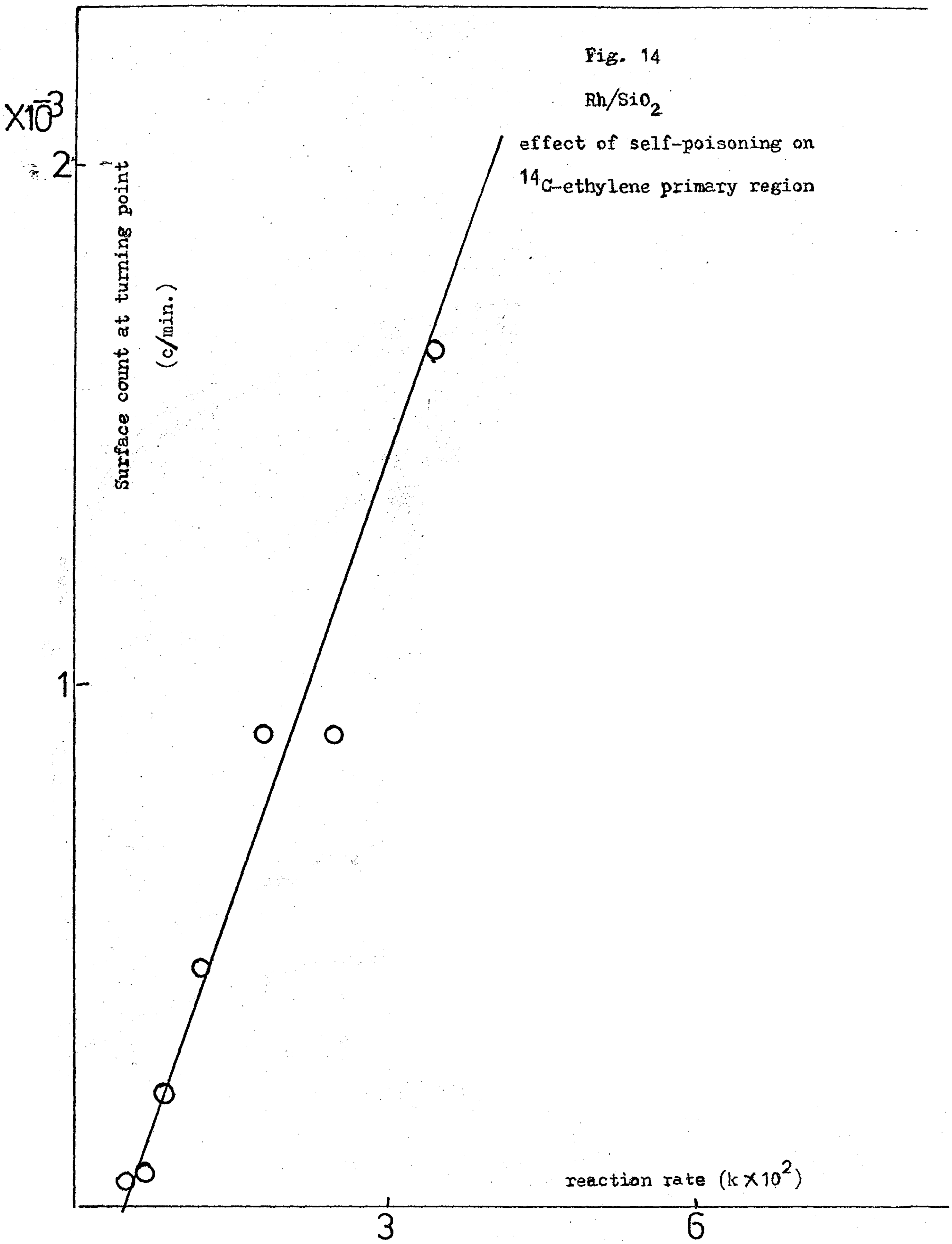


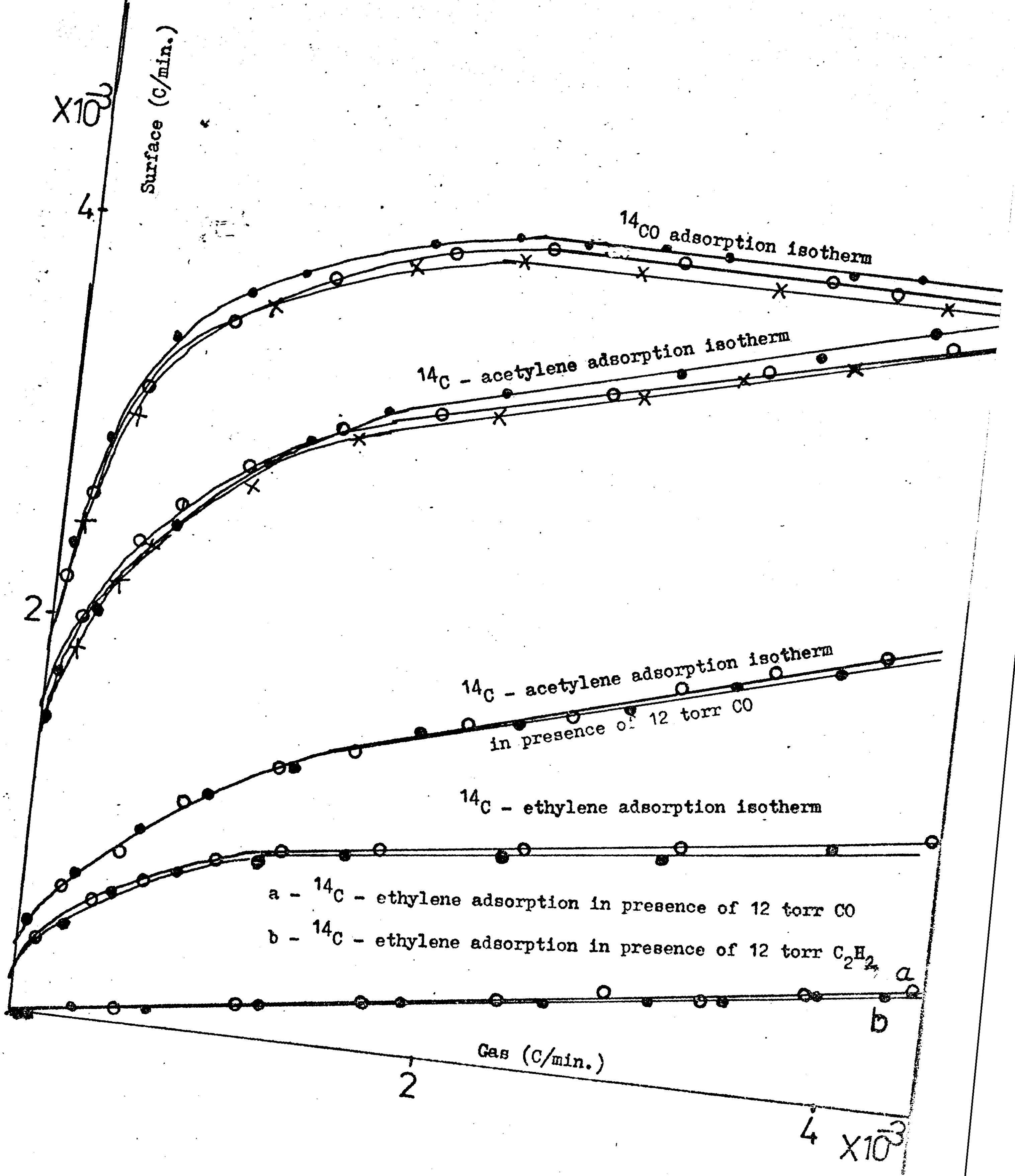
Fig. 14

Rh/SiO$_2$

effect of self-poisoning on ^{14}C-ethylene primary region

Fig. 15

Pd/SiO$_2$



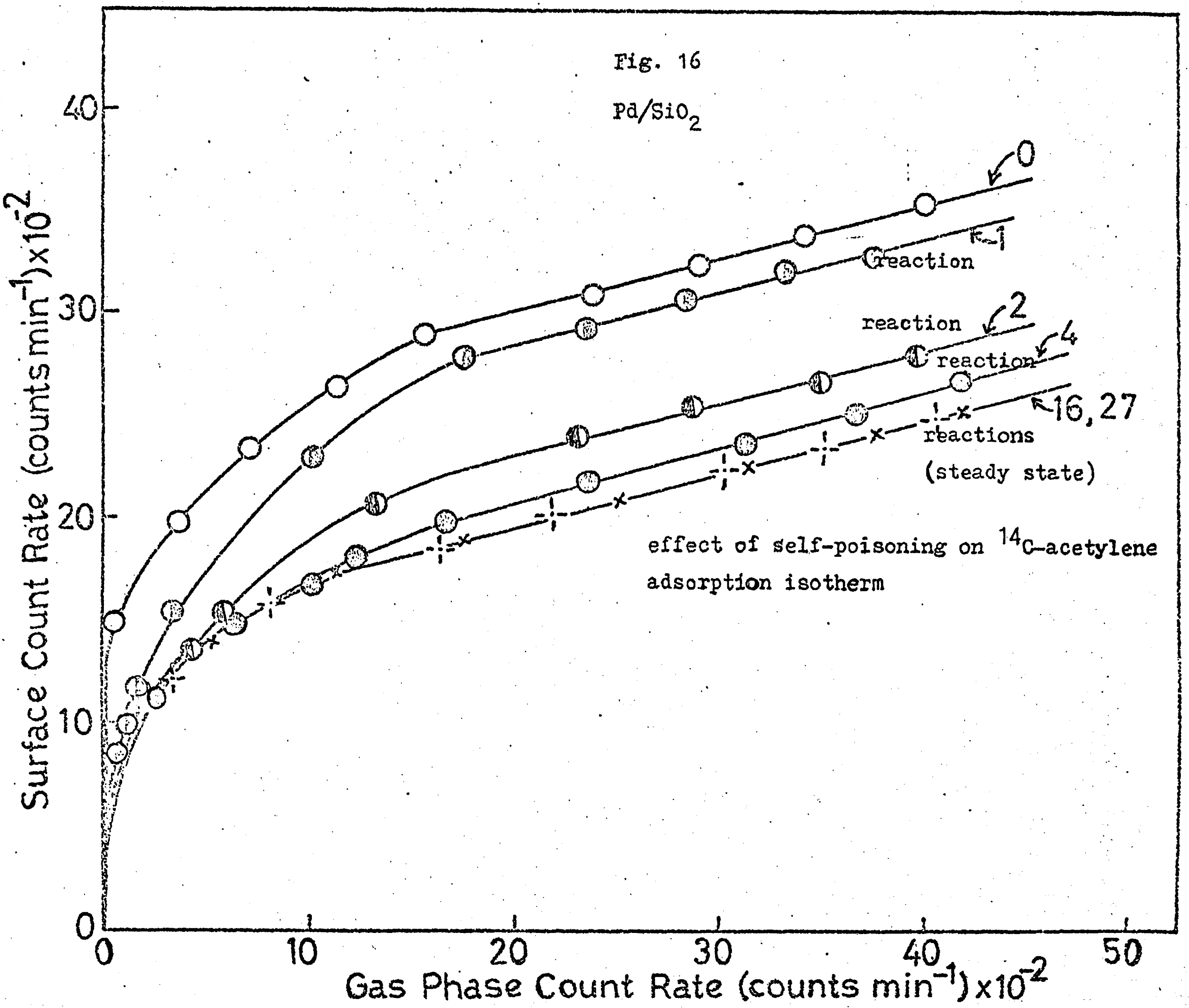


Fig. 16

Pd/SiO_2

effect of self-poisoning on ^{14}C-acetylene adsorption isotherm

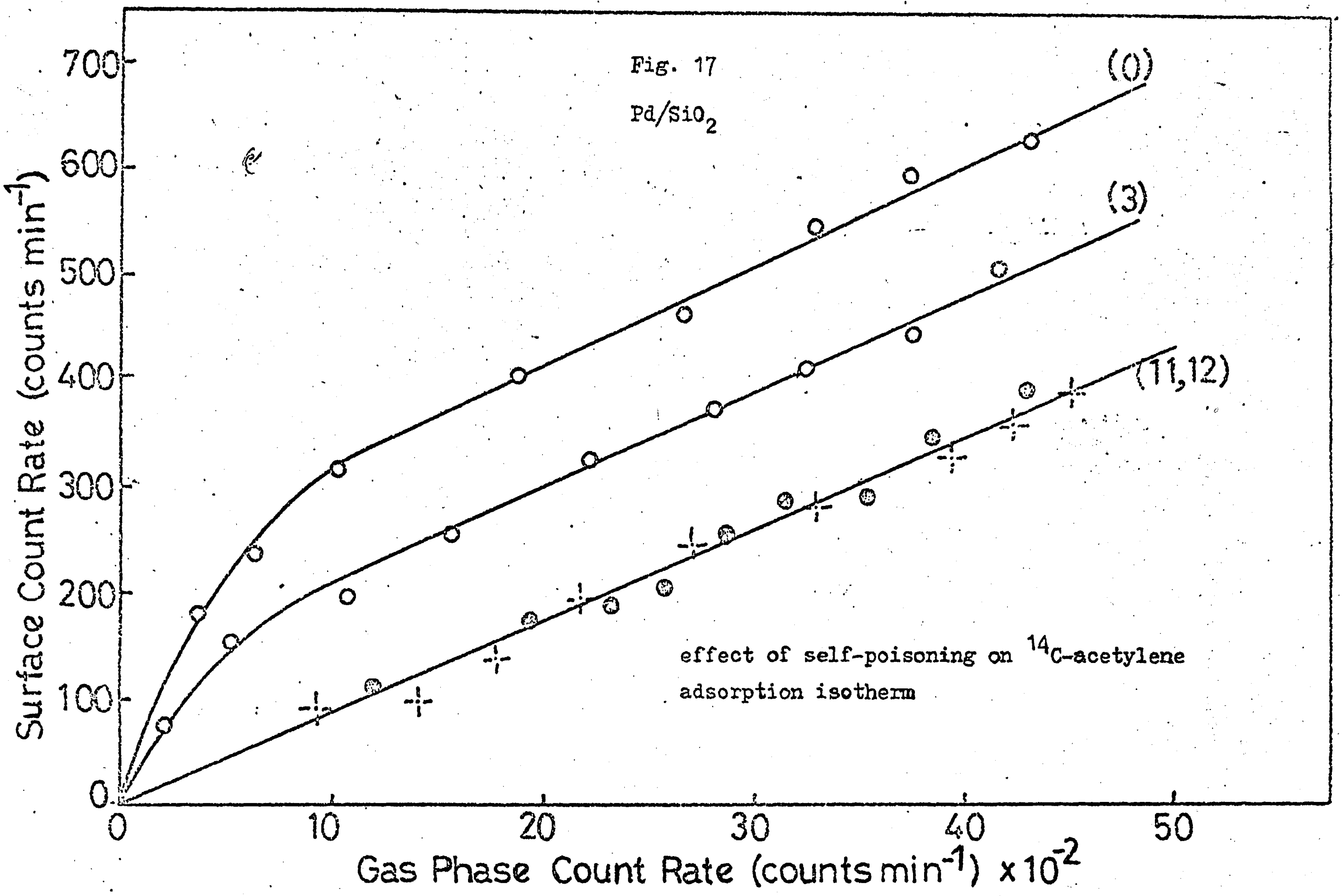


Fig. 17

Pd/SiO$_2$

effect of self-poisoning on ^{14}C-acetylene adsorption isotherm

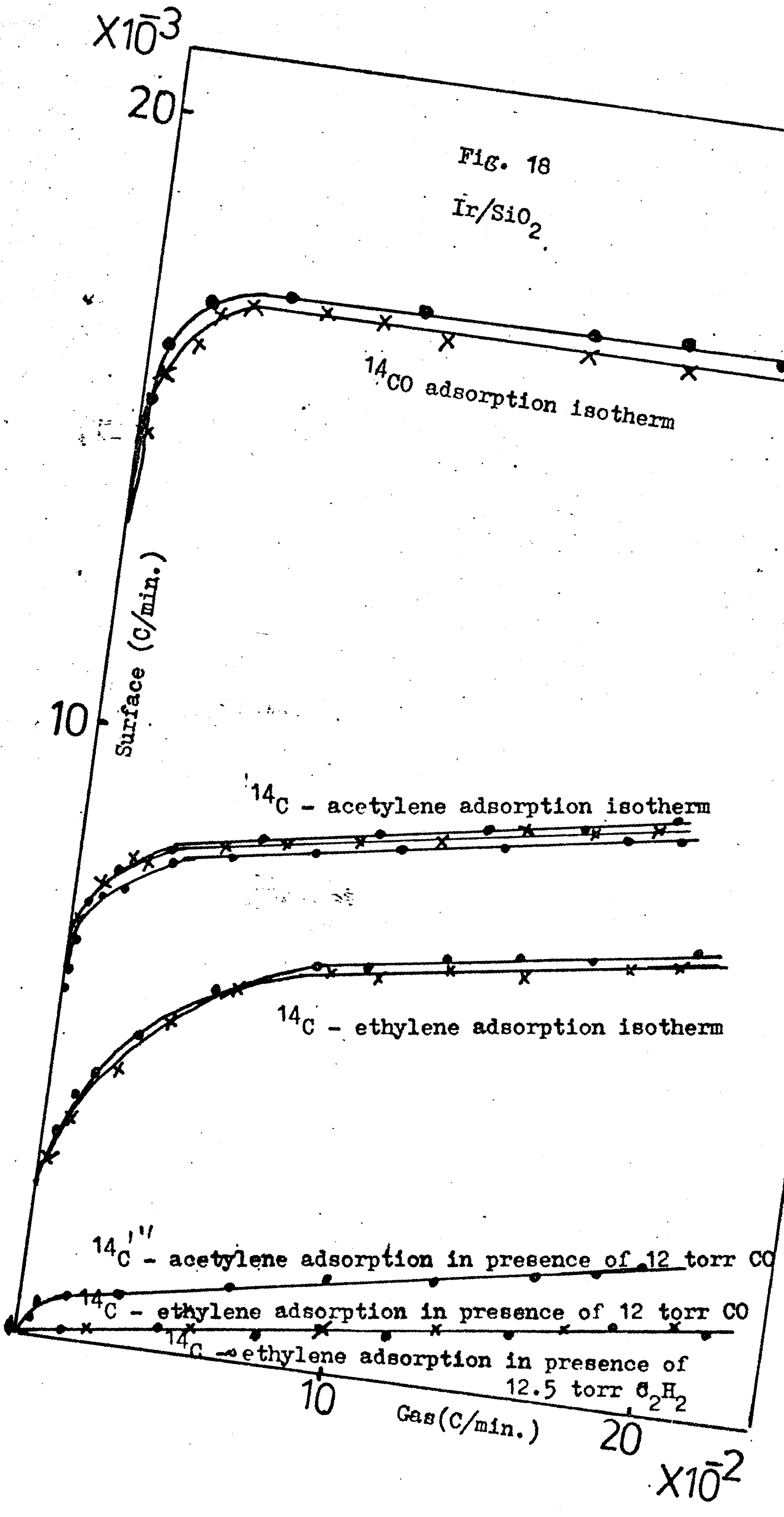


Fig. 18

Ir/SiO$_2$.

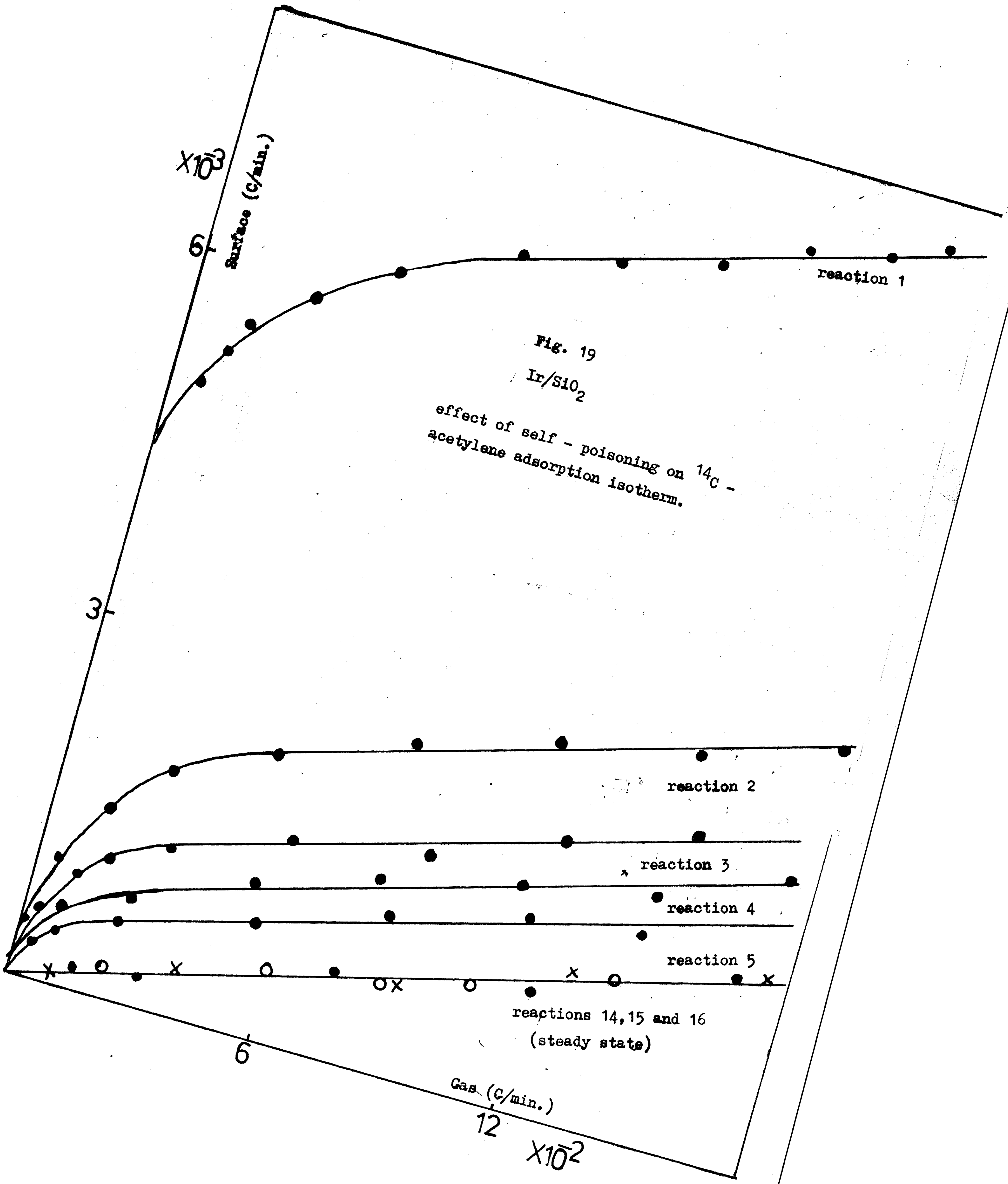


Fig. 19

Ir/SiO$_2$

effect of self - poisoning on ^{14}C - acetylene adsorption isotherm.

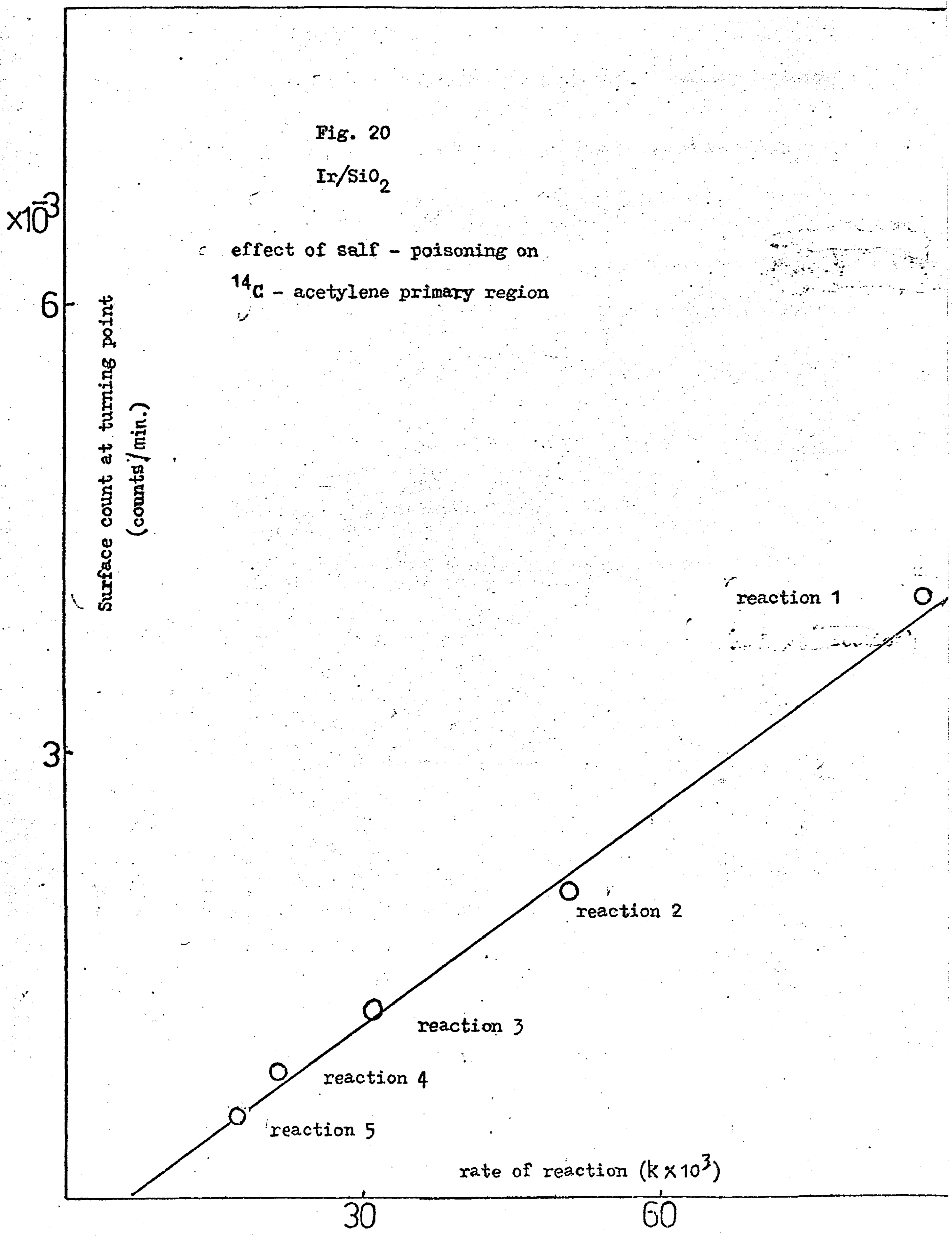


Fig. 20

Ir/SiO_2

effect of salf - poisoning on ^{14}C - acetylene primary region

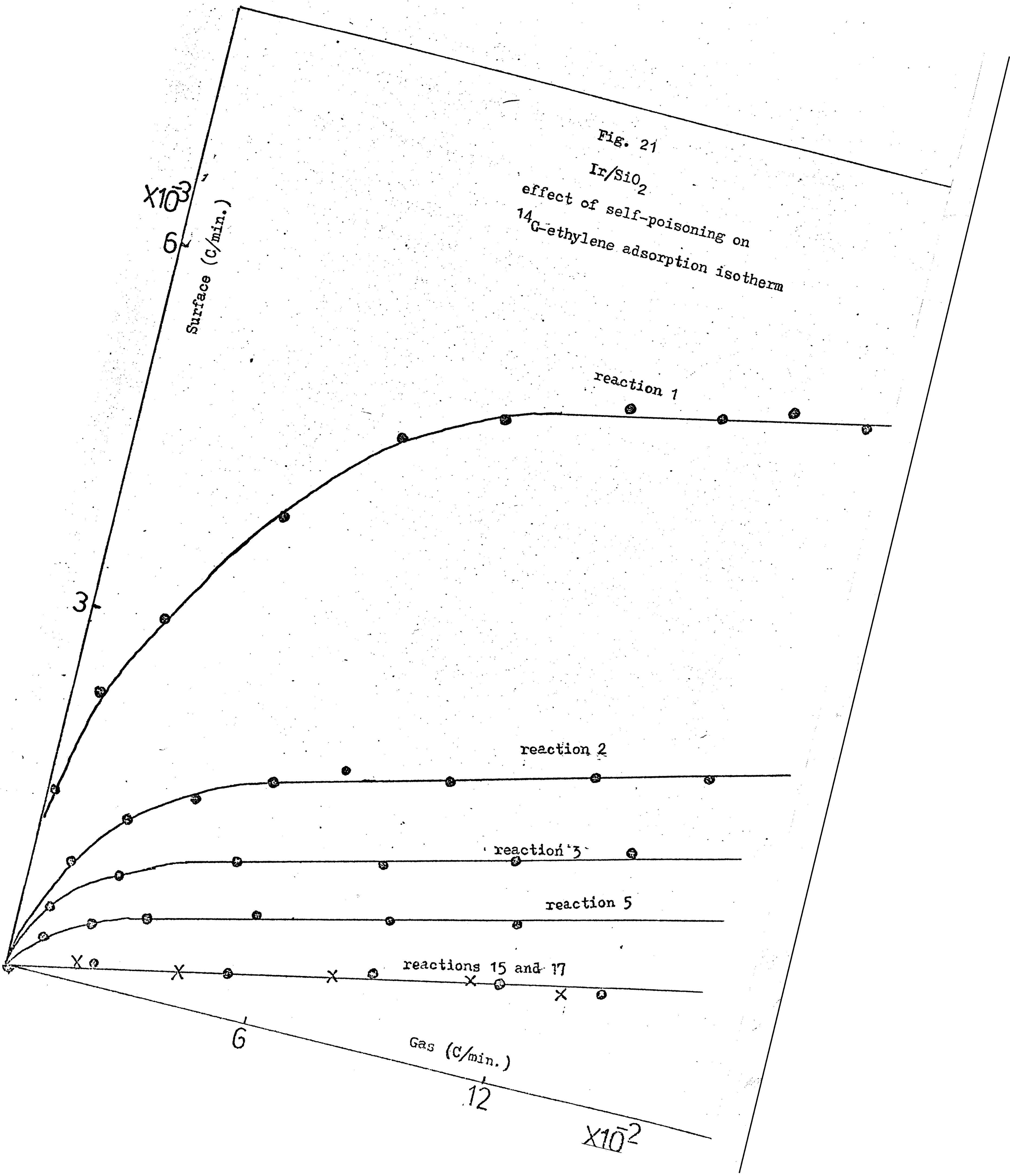


Fig. 21

Ir/SiO$_2$

effect of self-poisoning on

^{14}C-ethylene adsorption isotherm

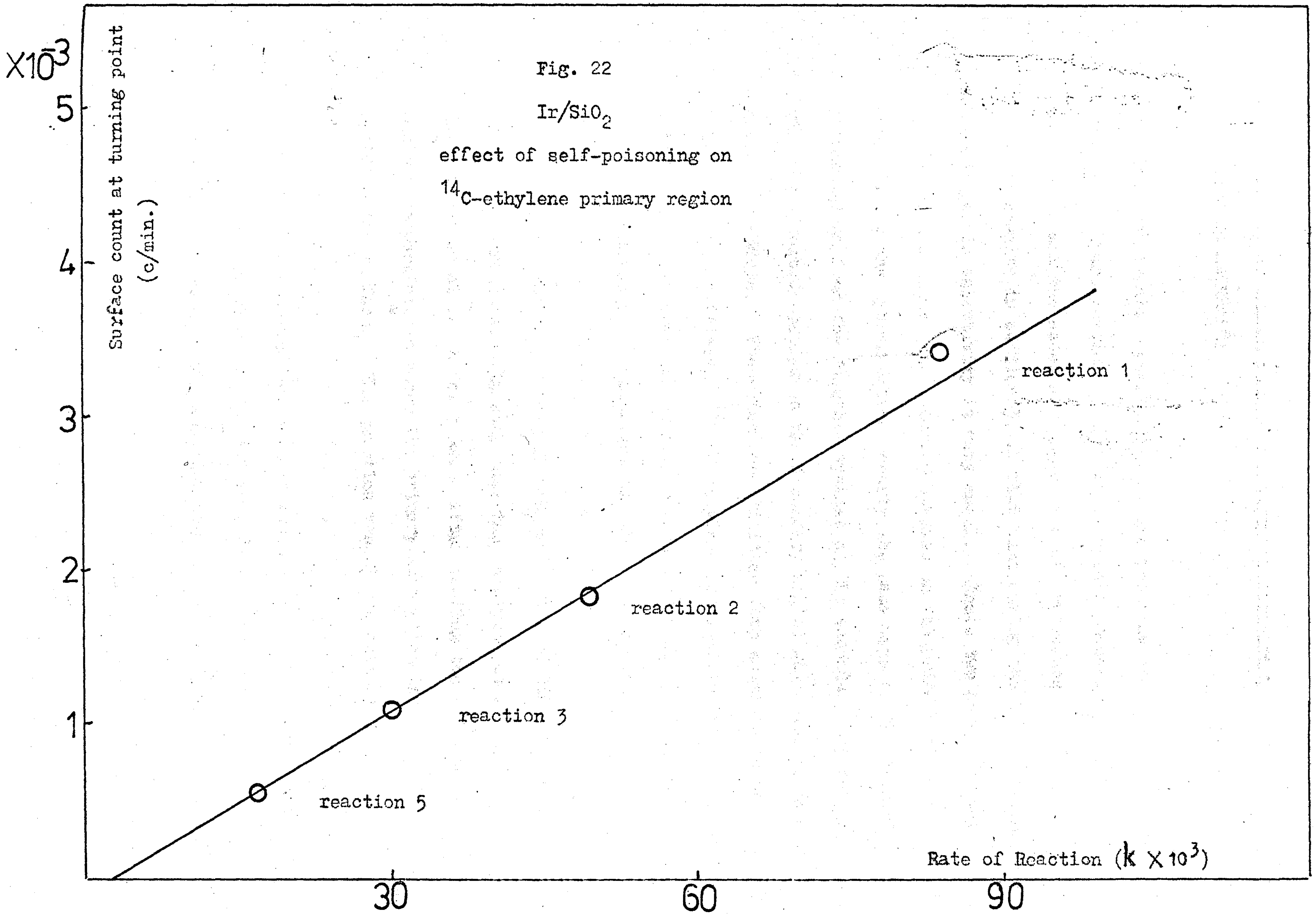


Fig. 22

Ir/SiO_2

effect of self-poisoning on

^{14}C-ethylene primary region

3.2 The Chemical Nature and the Catalytic Activity of the Adsorbed Species.

The experimental observations in the previous sections show that in the hydrogenation of acetylene, species adsorbed on both the primary and the secondary region are of importance.

The results in section 3.1.2 show that during the deactivation, the changes in selectivity is very small. These two observations suggest that either: the adsorbed species on the primary region give, during the hydrogenation, nearly the same type of the products as that given from the adsorbed species on the secondary region, or, only the adsorbed species on the secondary region give rise to the reaction products. These two possibilities were examined in the following way; sufficient ^{14}C - acetylene was admitted to the catalyst to just cover the primary region. A C_2H_2 - H_2 mixture was then admitted to the catalyst and the products analyzed for radioactivity.

0.2 g. of Rh/SiO_2, 0.51 g Ir/SiO_2 and 0.1 g Pd/SiO_2 were used in these experiments. In each case the catalyst was reduced and then evacuated at 623 K for 6 hr. After cooling the catalyst to ambient temperature in vacuo the primary adsorption isotherm was build on the surface. The reaction vessel was evacuated for one hr. to remove the gas phase radioactivity. No decrease in surface count rate was observed during this evacuation. A pre-mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel. The reaction was allowed to proceed to about 40% conversion and a sample was extracted from the reaction vessel for analysis. The radioactivity in ethylene and ethane products was determined. The analysis showed that, with all three catalysts the ^{14}C - acetylene adsorbed on the primary region appeared only as ^{14}C - ethane.

The chemical nature of the species, which were removed during the hydrogenation from the secondary region, was examined by covering first the primary region with non - radioactive acetylene followed by covering a sufficient part of the secondary region with ^{14}C - acetylen (specific activity = 0.1 m Ci/mM). The reaction vessel was evacuated for one hr. A pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel. The reaction was allowed to proceed until 40% conversion, after which the content of the reaction vessel was expanded to a one litre storage vessel. The reaction products in the storage vessel were condensed by liquid nitrogen and freed from hydrogen. A sample from the products was condensed into the chromatography sample system taking into account that the amount of the condensed products is sufficient to give a reasonable number of counts in ethylene and ethane peaks.

The number of counts in the ethylene and ethane peaks was determined in the proportional counter. In the case of Rh/SiO_2 table 7 shows that both $^{14}C_2H_4$ and $^{14}C_2H_6$ was produced from the secondary region and the selectivity calculated by

$$S = \frac{^{14}C_2H_4}{^{14}C_2H_4 + {}^{14}C_2H_6}$$

is equal to the value of the selectivity as determined, using a catalyst in the steady state, by the formula:

$$S = \frac{P\,^{12}C_2H_4}{P\,^{12}C_2H_4 + P\,^{12}C_2H_6}$$ where P is the partial pressure of the non radioactive C_2H_4 or C_2H_6

Similar results were obtained using Ir/SiO_2 and Pd/SiO_2 (table 7).

Table 7

Catalyst	^{14}C - ethane	^{14}C - ethylene	$S = \frac{P^{12}C_2H_4}{P^{12}C_2H_4 + P^{12}C_2H_6}$ (steady state)	$S^* = \frac{^{14}C_2H_4}{^{14}C_2H_4 + {}^{14}C_2H_6}$
Rh/SiO_2	5003	15314	0.754	0.7538
Pd/SiO_2	804	18851	0.94	0.959
	742	17938		0.960
Ir/SiO_2	16805	3263	0.163	0.1626
	17528	3416		0.1631

These results show that the species which is located on the secondary region is responsible for the formation of the reaction products during hydrogenation. Experiments, by means of which the chemical nature of the adsorbed species (i.e. associatively or dissociatively adsorbed) can be investigated were performed as follows:

A freshly reduced catalyst evacuated at 623 K for 6 hr. and cooled in vacuo to ambient temperature were used. A small amount of ^{14}C - acetylene was introduced to the reaction vessel. After each addition a sample from the gas phase, in contact with the surface, was analyzed.

This process was repeated several times until all the primary region and a sufficient part of the secondary region was covered. A similar experiment was performed using ^{14}C - ethylene.

In the case of Rh/SiO_2 the analysis of the gas phase in equilibrium with the surface at various stages during the adsorption of ^{14}C - acetylene showed that during the build up of the primary region the gas phase was solely ethane. This information of ethane ceased at the onset of the secondary adsorption. No ethylene was observed to be formed at any stage during the adsorption of acetylene (Figure 23).

Similar analysis during the ^{14}C - ethylene adsorption showed that only ethane was present in the gas phase during the build up of the primary region; ethylene only appeared in the gas phase at the commencement of the secondary region. The formation of ethane ceased at the onset of the secondary region (Figure 24).

Similar results were obtained with Ir/SiO_2 (Figures 25 and 26).

Fig.23

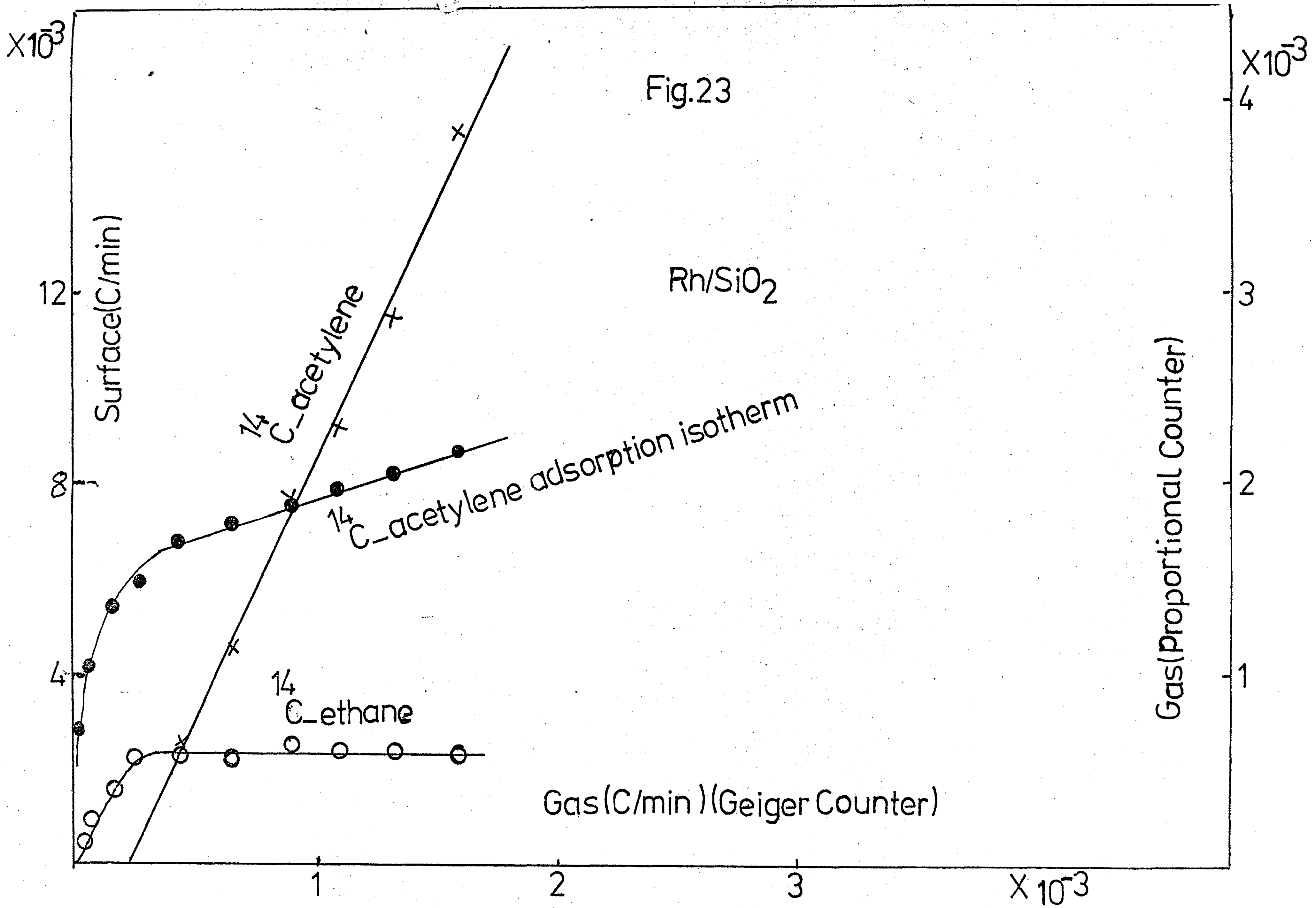
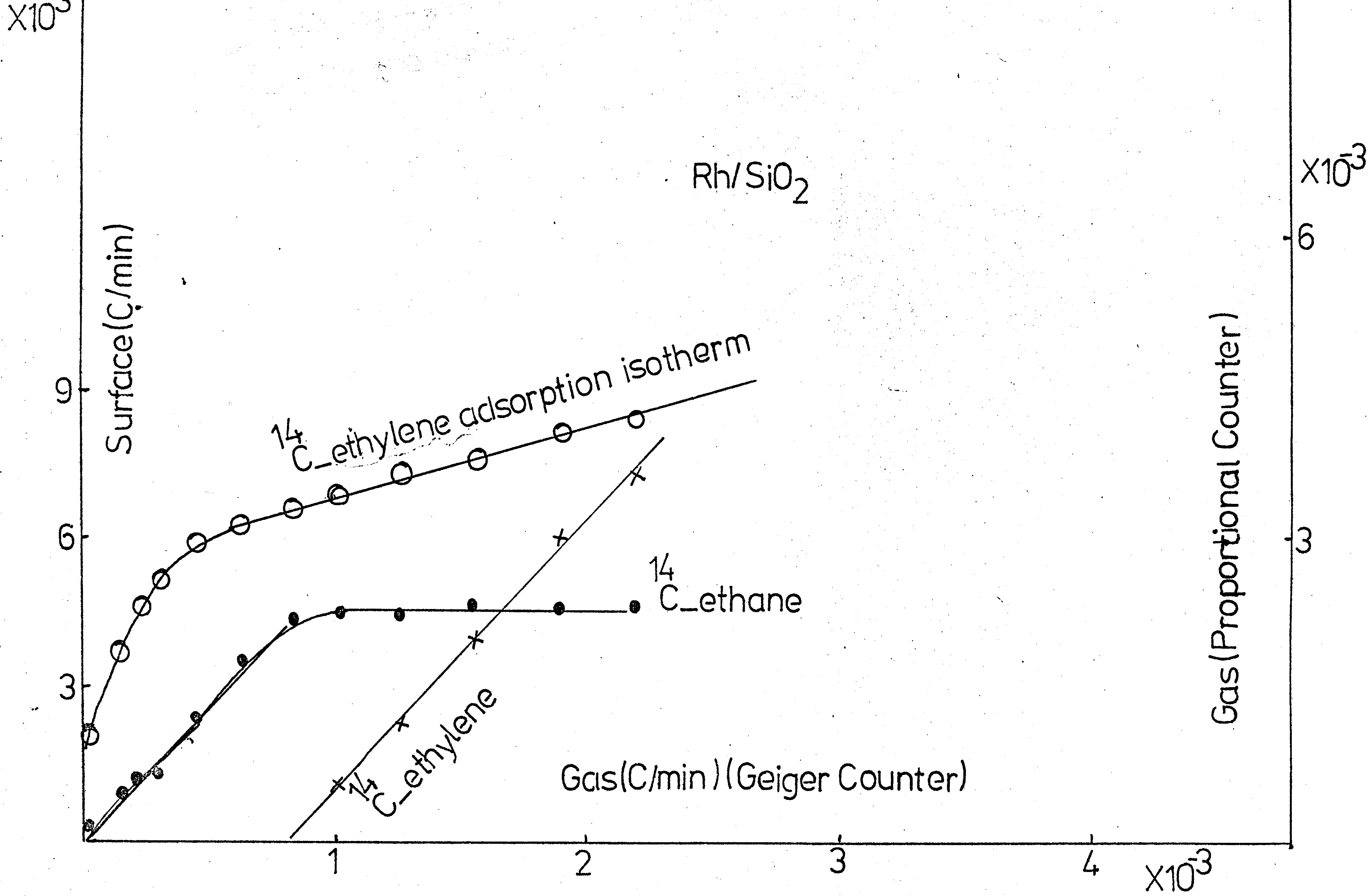

Rh/SiO$_2$
$\times 10^{-3}$
Surface(C/min)
12
8
4
$\times 10^{-3}$
4
3
2
1
Gas(Proportional Counter)
^{14}C_acetylene
^{14}C_acetylene adsorption isotherm
^{14}C_ethane
Gas(C/min)(Geiger Counter)
1
2
3
$\times 10^{-3}$

Fig.24.


Rh/SiO$_2$
Surface(C/min)
$\times 10^{-3}$
9
6
3
Gas (Proportional Counter)
$\times 10^{-3}$
6
3
^{14}C_ethylene adsorption isotherm
^{14}C_ethane
^{14}C_ethylene
Gas(C/min) (Geiger Counter)
1
2
3
4
$\times 10^{-3}$

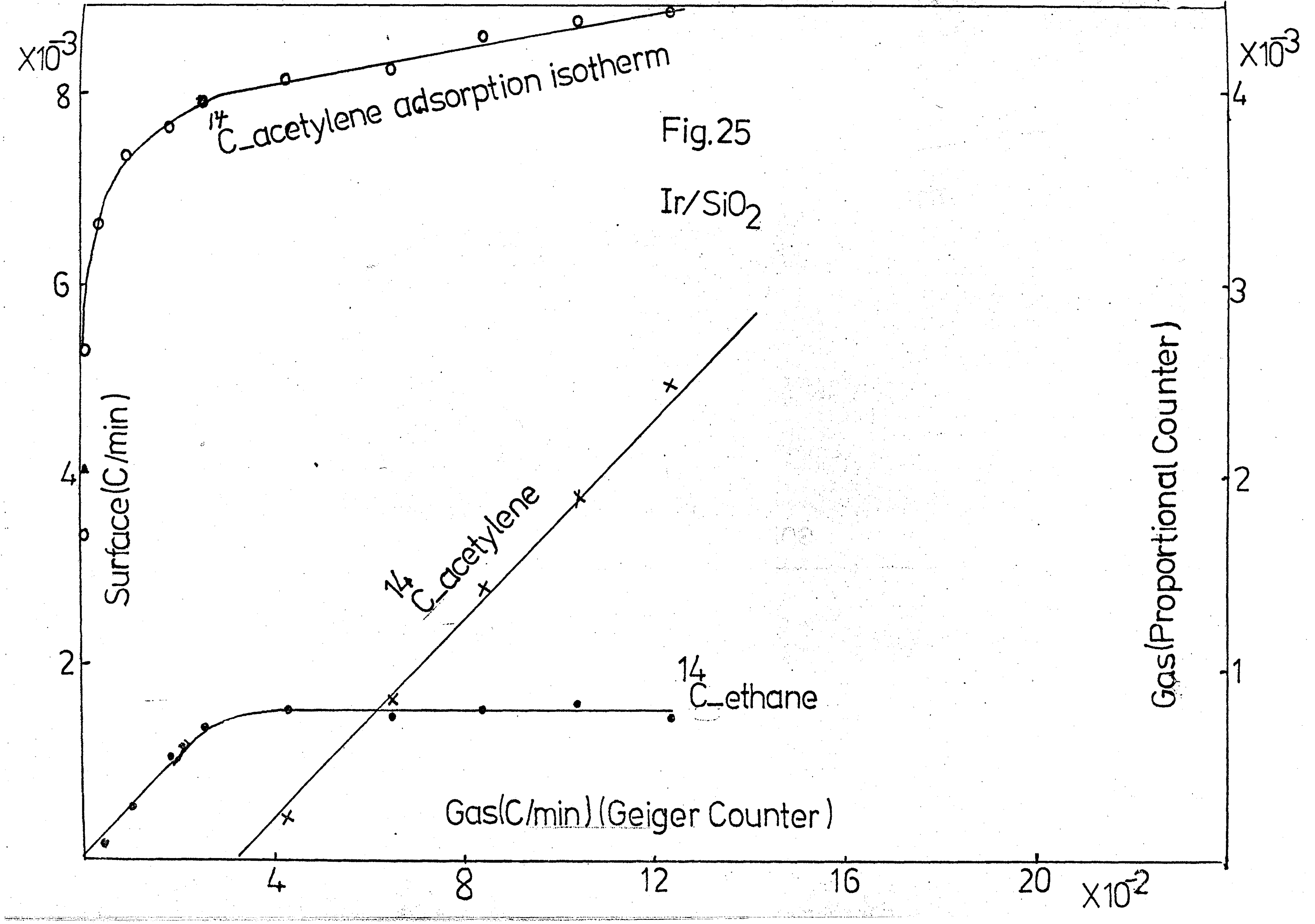


Fig. 25

Ir/SiO$_2$
^{14}C_acetylene adsorption isotherm
^{14}C_acetylene
^{14}C_ethane
Surface (C/min)
X10^{-3}
2
4
6
8
Gas (Proportional Counter)
X10^{-3}
1
2
3
4
Gas (C/min) (Geiger Counter)
X10^{-2}
4
8
12
16
20

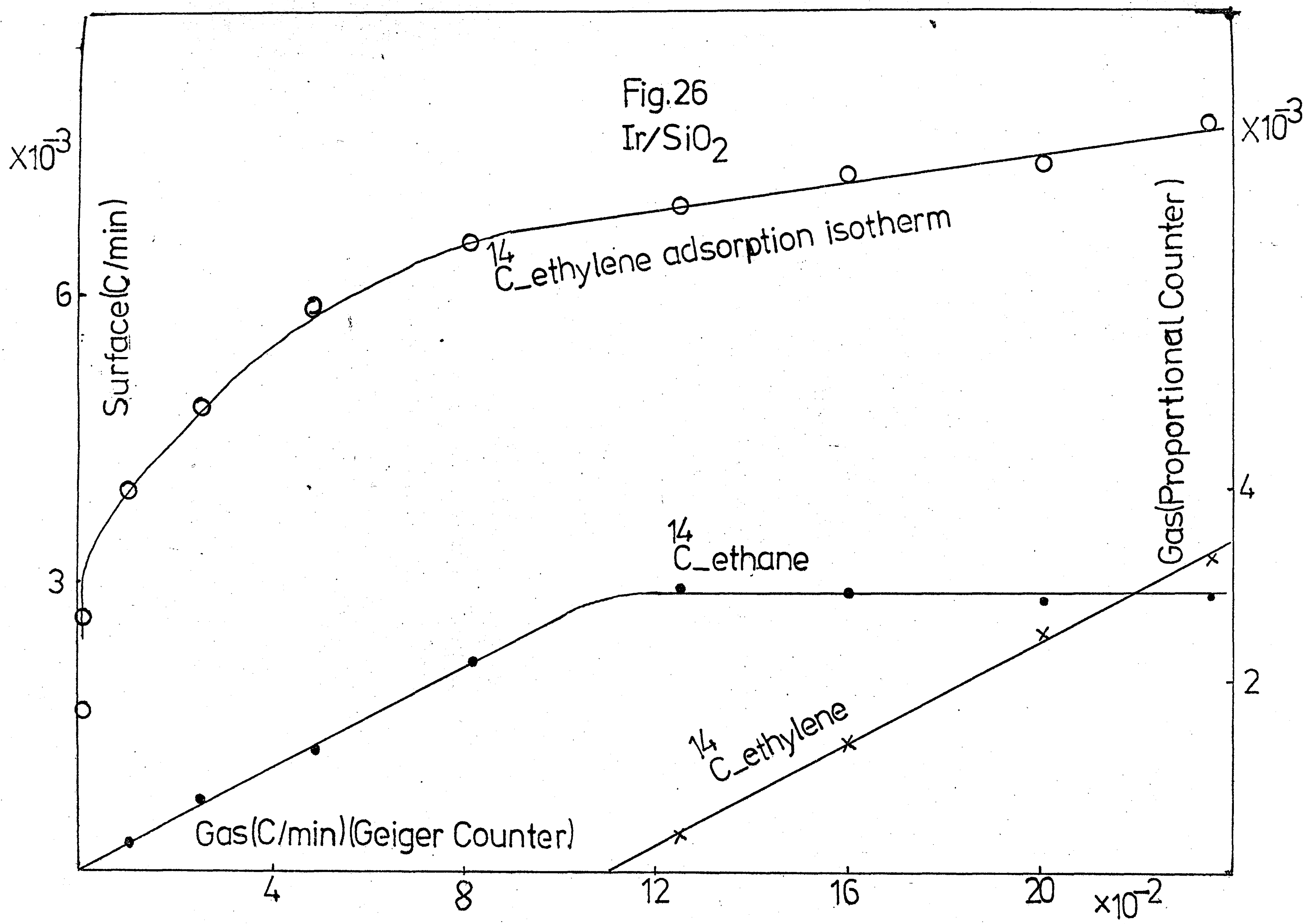


Fig.26

Ir/SiO$_2$

With ^{14}C - acetylene over Pd/SiO_2 ethane was the only gaseous species present up to a point corresponding to 80.5% of the total primary adsorption region. During the subsequent build up of the isotherm the gas consisted of the ethane, formed in the primary region, and acetylene. No ethylene was observed to be formed at any stage during the adsorption of acetylene (Figure 27).

With ^{14}C - ethylene over Pd/SiO_2, the gas in equilibrium with the primary adsorbed species also consisted entirely of ethane. Ethylene only appeared in the gas phase at the commencement of the secondary region.

The formation of ethane ceased at the onset of the secondary region. (Figure 28).

The same set of experiments was repeated on Ir/SiO_2, Rh/SiO_2 and Pd/SiO_2 which were deactivated by self poisoning to their steady states. In these experiments the analysis showed that, during the build up of ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms, no ^{14}C - ethane was present in the gas phase.

These results are consistent with dissociative adsorption occuring on the primary region, while only associative adsorption takes place on the secondary region on either the freshly reduced and the steady state catalysts.

FIG.27

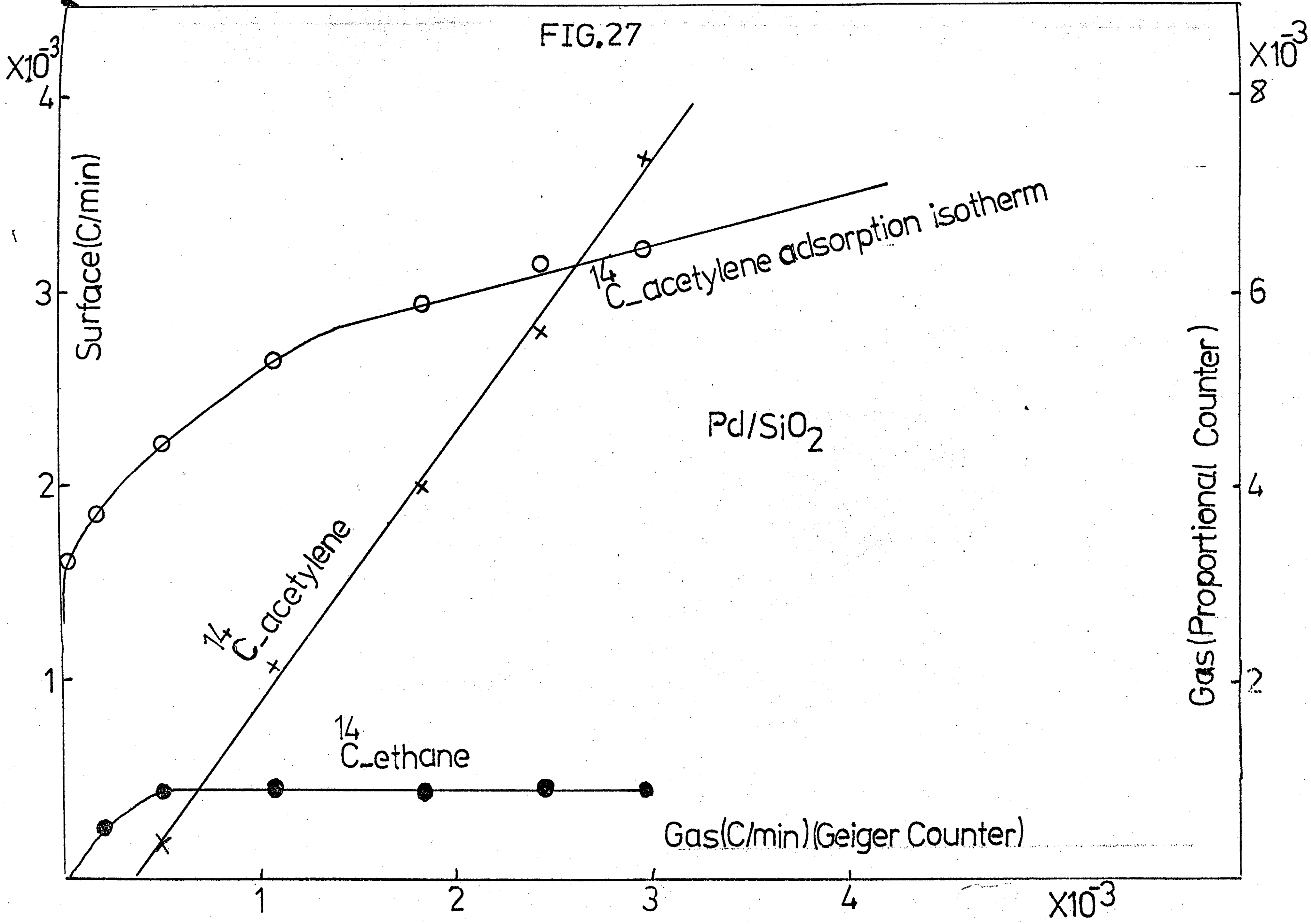
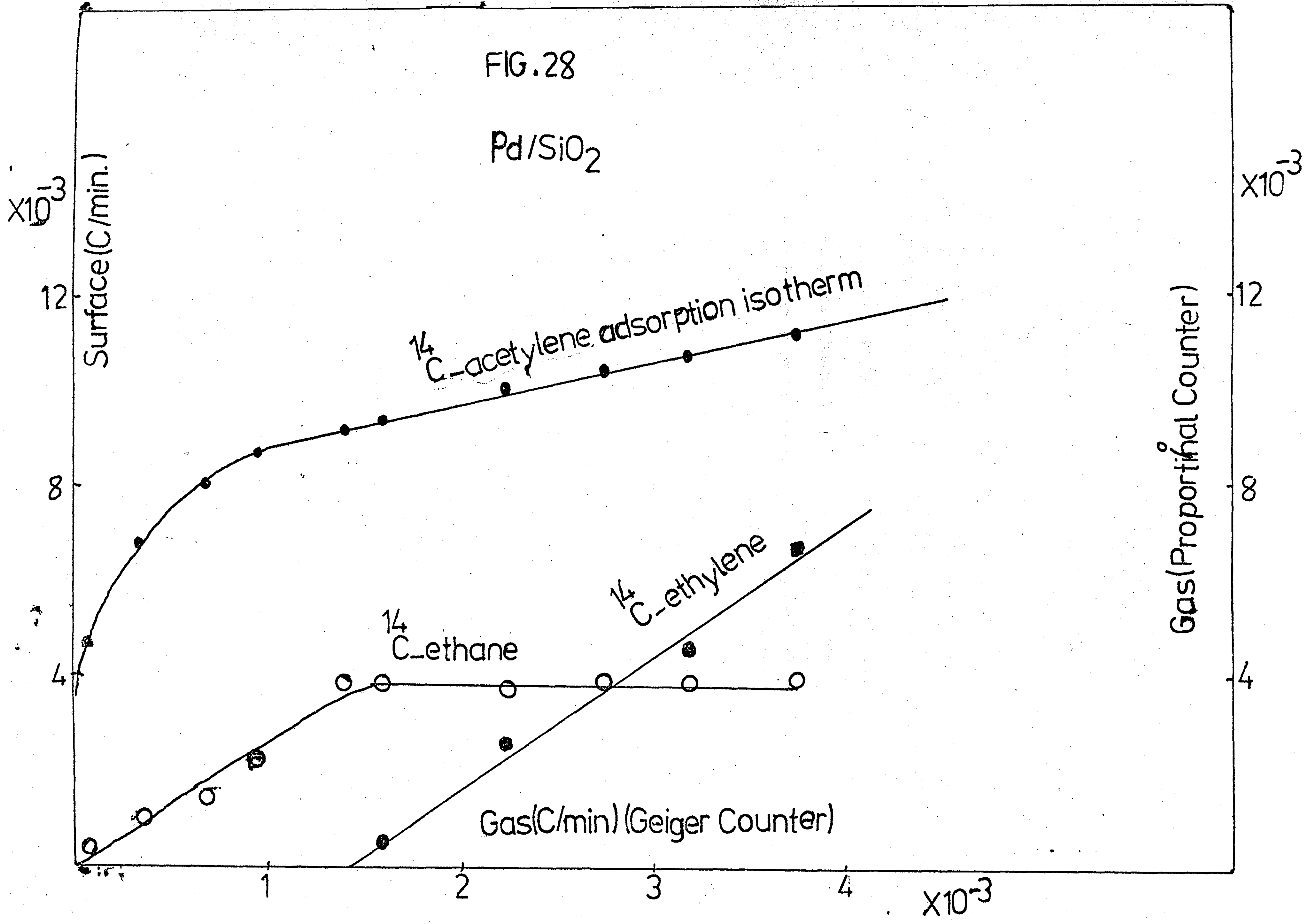

X10^{-3}
4
3
2
1
Surface(C/min)
X10^{-3}
8
6
4
2
Gas(Proportional Counter)
^{14}C_acetylene adsorption isotherm
^{14}C_acetylene
Pd/SiO$_2$
^{14}C_ethane
Gas(C/min)(Geiger Counter)
1
2
3
4
X10^{-3}

FIG.28


Pd/SiO$_2$
Surface(C/min.)
X10^{-3}
12
8
4
^{14}C_acetylene adsorption isotherm
^{14}C_ethane
^{14}C_ethylene
Gas(C/min) (Geiger Counter)
1
2
3
4
X10^{-3}
Gas(Proportional Counter)
X10^{-3}
12
8
4

3.3 Self poisoning at elevated temperature.

It was found in this work (section 3.1.3) that the catalytic activity of the freshly reduced catalyst could be reproducibly restored by heating the deactivated catalyst in an atmosphere of hydrogen for one hr. at 623 K. This shows that self poisoning is not caused by sintering of the metal; therefore it is reasonable to assume that self poisoning is caused by the formation of surface carbonaceous residues.

In order to justify this assumption, it was decided to deactivate a freshly reduced catalyst by self poisoning at high temperature in order to enhance the C - C bond fission reaction.

If self poisoning was caused by deposition of carbon and the formation of surface carbide, then self poisoning would have proceeded much faster at higher temperature. Rh/SiO_2 was selected as catalyst in this experiment because of its high activity for C - C cracking reaction. It was observed during this work that, at 473 K (using 0.1 g 5 % Rh/SiO_2), the cracking reaction of ethane (20 torr) in presence of 60 torr hydrogen proceeded rapidly leading to the formation of methane.

Ir/SiO_2 was found, during this work, to be less active than Rh/SiO_2 for C - C cracking reaction, although cracking of ethane (20 torr) in the presence of 60 torr hydrogen can take place at 623 K leading to the formation of methane.

Pd/SiO_2 is very poor catalyst for the cracking reaction because even at 623 K cracking of ethane in the presence of hydrogen proceeded only very slowly.

Using 0.021 g. Rh/SiO_2 at 373 K, the deactivation process was carried out as described above by introducing to the reaction vessel a pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen.

This process was repeated until a steady state constant activity was attained. Allowing for weights of catalyst figure 29 shows that deactivation at 100 °C proceeded much slower than the deactivation at room temperature (figure 3(a)).

This suggests that self poisoning is not caused by deposition of carbon and the formation of surface carbide.

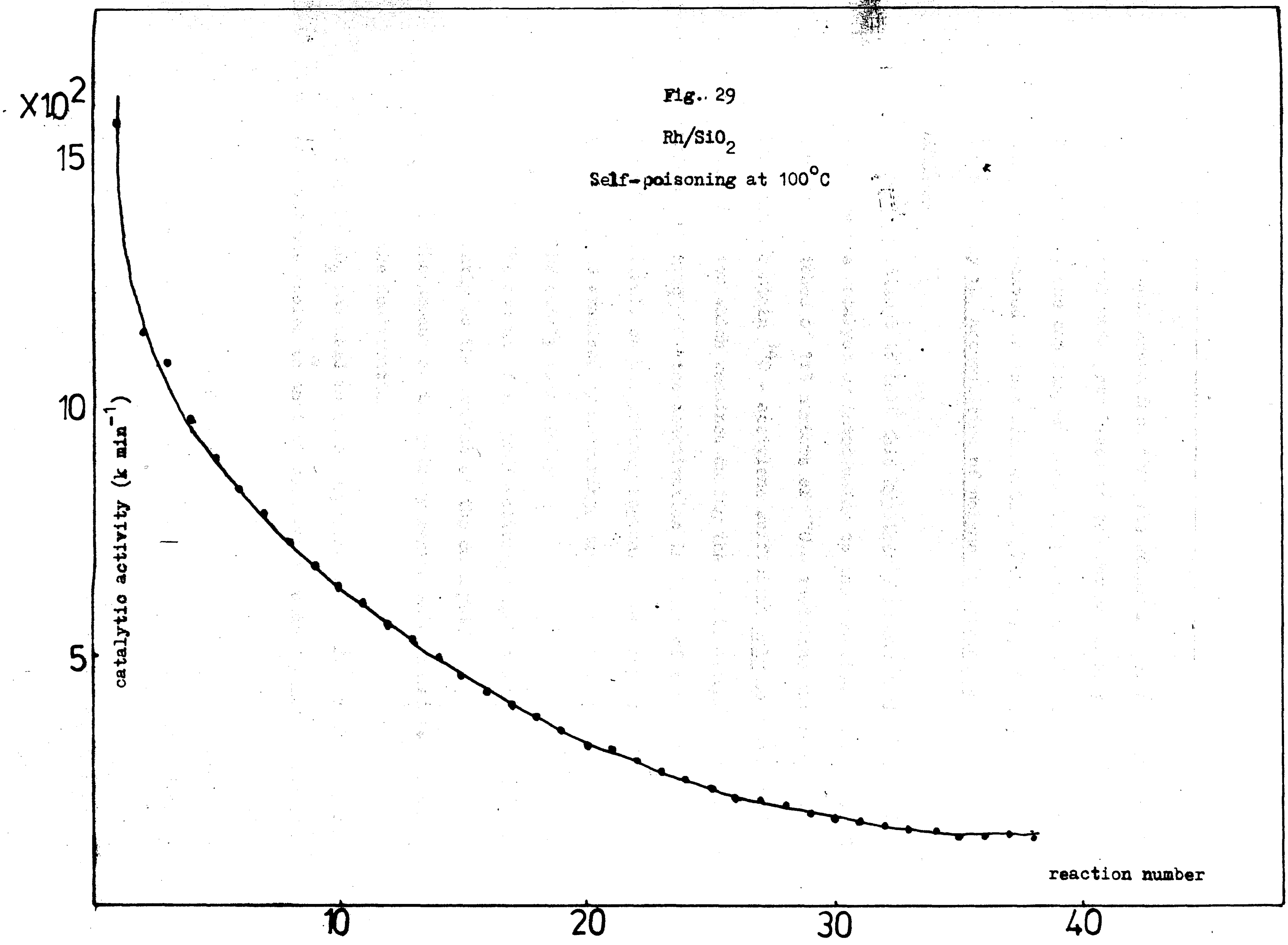


Fig. 29

Rh/SiO$_2$

Self-poisoning at 100°C

3.4 Deactivation by ^{14}C - acetylene /H_2 mixture.

It is a well known fact that the adsorption of acetylene on different metal catalysts leads to the formation of polymeric species. Accordingly, one can suppose that the phenomena of self - poisoning which is observed in this work with Rh/SiO_2, Ir/SiO_2 and Pd/SiO_2 may be caused by the accumulation of polymeric species on the primary region.

In an attempt to test this hypothesis it was decided to deactivate the catalyst by introducing to the reaction vessel small separate batches of 1:3 mixture of ^{14}C - acetylene and hydrogen. Each batch contain ^{14}C - acetylene sufficient only to cover the primary region which remained during the deactivation. By this way one can examine the deactivation in terms of the processes occuring entirely on the primary region. The progress of self - poisoning was examined by measuring, during the deactivation:

(1) The catalytic activity.

(2) The amount of the radioactivity which accumulated permanently on the surface of the catalyst.

(3) The amount of the primary region which remained during the deactivation.

0.2 g Rh/SiO_2 was used in these experiments. After reduction the catalyst was cooled to ambient temperature under hydrogen, and then evacuated for one hr. The turning point (i.e. the amount) of the ^{14}C - acetylene (specific activity = 0.1 mCi/mM) primary region was determined and the catalyst reactivity was measured using a mixture of 12.5 torr acetylene with 37.5 torr hydrogen. The amount of ^{14}C - acetylene (specific activity = 0.1 mCi/mM) which was required to cover the primary region alone in this case was determined and found to be 0.53 torr (equivalent to 0.944×10^{19} acetylene molecules, including the gas phase in equilibrium with the primary region).

The following experiments were performed:-

Experiment 1.

The catalyst was cleaned by hydrogen for 4 hr. at 623 K, then was allowed to cool to ambient temperature before evacuation for 1 hr. A sample of 1:3 ^{14}C - acetylene and hydrogen was introduced to the reaction vessel. The quantity of ^{14}C - acetylene (specific activity = 0.1 mCi/mM) in this sample was 0.32 torr which is sufficient to cover only 60% of the primary region. After 3 min. the reaction vessel was evacuated and another sample, containing the same quantity of ^{14}C - acetylene as in the first sample was introduced to the reaction vessel. This process was repeated several times until the total number of samples admitted was 9. The catalyst was allowed to stand for one hr. under the reaction products of the last sample, and then evacuated for 1 hr.

The retained surface radioactivity (i.e. the amount of the poison) was measured. The ^{14}C - acetylene adsorption isotherm on the used catalyst was determined in order to evaluate the turning point of the primary region. The catalyst activity was then measured by introducing a pre-mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen to the reaction vessel and measuring the first order rate constant (k min^{-1}) of the reaction.

Experiment 2.

The catalyst from experiment 1 was cleaned by a stream of hydrogen for 4 hr. at 623 K. After cooling to ambient temperature under hydrogen the catalyst was evacuated for one hr.

Using exactly the same procedure as in experiment 1, 18 samples of 1:3 ^{14}C - acetylene and hydrogen were introduced to the reaction vessel, each sample containing ^{14}C - acetylene sufficient to cover only 60% of the primary region. The catalyst was allowed to stand for one hr. under the reaction products of the last sample, and then evacuated for one hr.

The retained surface radioactivity (i.e. amount of the poison), the turning point of ^{14}C - acetylene primary region and the catalyst activity were measured after the deactivation in the same way as for experiment 1.

Experiment 3.

The catalyst from experiment 2 was cleaned as in the previous experiments. The catalyst was deactivated using 18 batches of 1:3 ^{14}C - acetylene and hydrogen, each batch containing ^{14}C - acetylene sufficient to cover 60% of the primary region followed by a further 37 samples of the same mixture each sample containing ^{14}C - acetylene sufficient to cover 40% of ^{14}C - acetylene primary region.

The retained surface radioactivity, the turning point of the primary region, and the catalytic activity were measured after the deactivation as in the previous experiments.

Experiment 4.

The catalyst was cleaned as in the previous experiments. The catalyst was deactivated by 18 samples of 1:3 ^{14}C - acetylene and hydrogen each sample containing ^{14}C - acetylene sufficient to cover 60% of ^{14}C - acetylene primary region followed by 37 samples of the same mixture each sample containing sufficient ^{14}C - acetylene to cover 40% of the primary region and then finally by 200 samples of the same mixture each containing sufficient ^{14}C - acetylene to cover 15% of the primary region.

The retained surface radioactivity (i.e. the amount of the poison), the ^{14}C - acetylene primary region and the catalytic activity were measured after the deactivation as in the previous experiments.

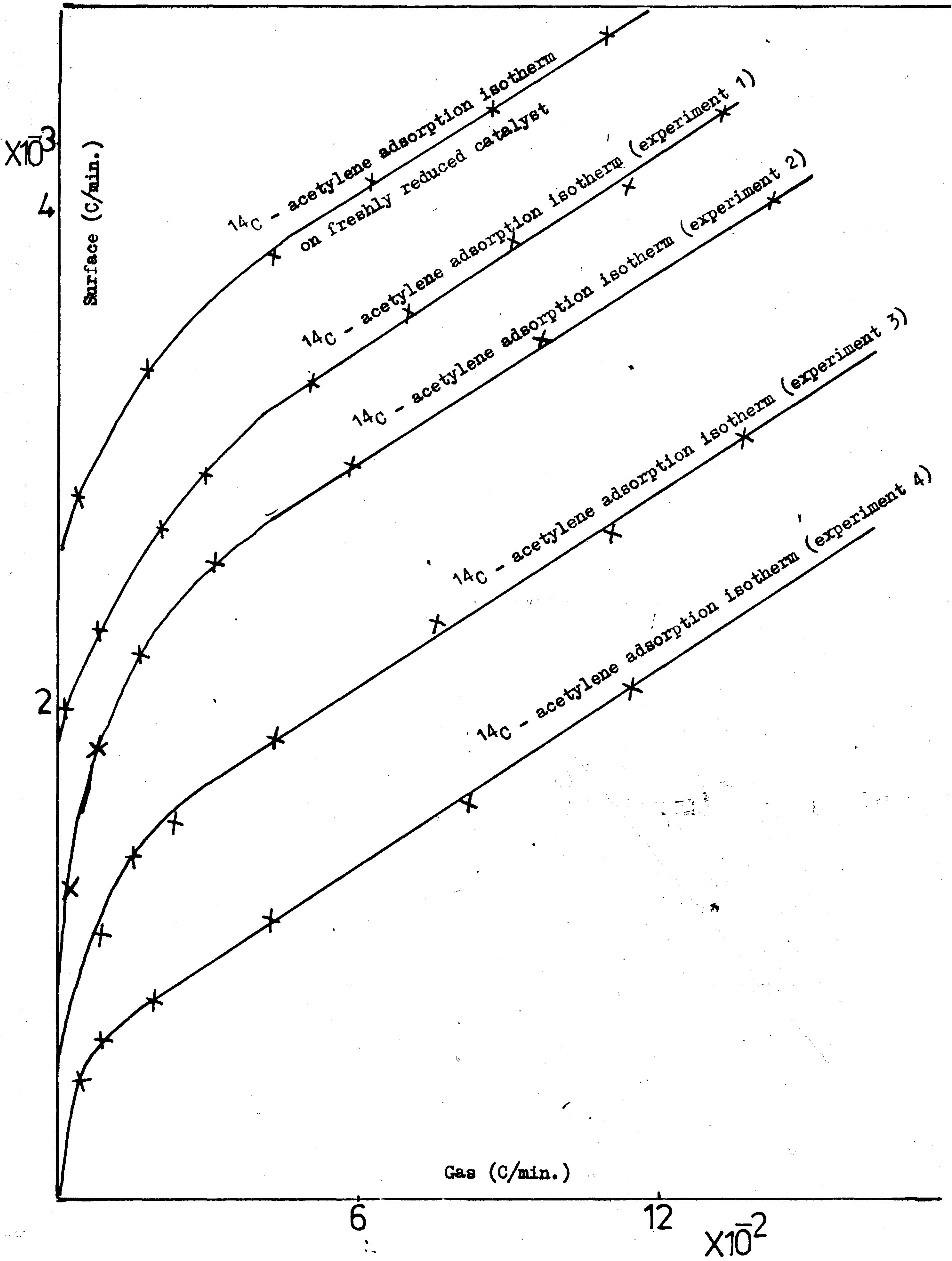
The results of these experiments are summarized in table 8 and figure 30. The results show that the deactivation is accompanied by a build up of permanently retained radioactive species on the surface. Figure 31 shows that the plot of the catalyst activity against the amount of these retained species yields a straight line with a negative slope, indicating that these retained species are effectively acting as a poison.

Table 8 shows that the sum of the retained radioactivity and the primary region over the poisoned catalyst is always larger than the primary region on the freshly reduced catalyst. This suggests that the deactivation is caused by the accumulation of surface polymeric species.

Figure 30 shows that deactivation was accompanied by a diminution in primary region, but was without any effect on the secondary region.

Figure 32 shows that the plot of the turning point of the primary region against the catalytic activity during the deactivation gives a straight line. The results in this section also give direct evidence that self poisoning takes place on the primary region.

Fig. 30



14C - acetylene adsorption isotherm
on freshly reduced catalyst
14C - acetylene adsorption isotherm (experiment 1)
14C - acetylene adsorption isotherm (experiment 2)
14C - acetylene adsorption isotherm (experiment 3)
14C - acetylene adsorption isotherm (experiment 4)
Surface (C/min.)
X10̄3
4
2
Gas (C/min.)
6
12
X10̄2

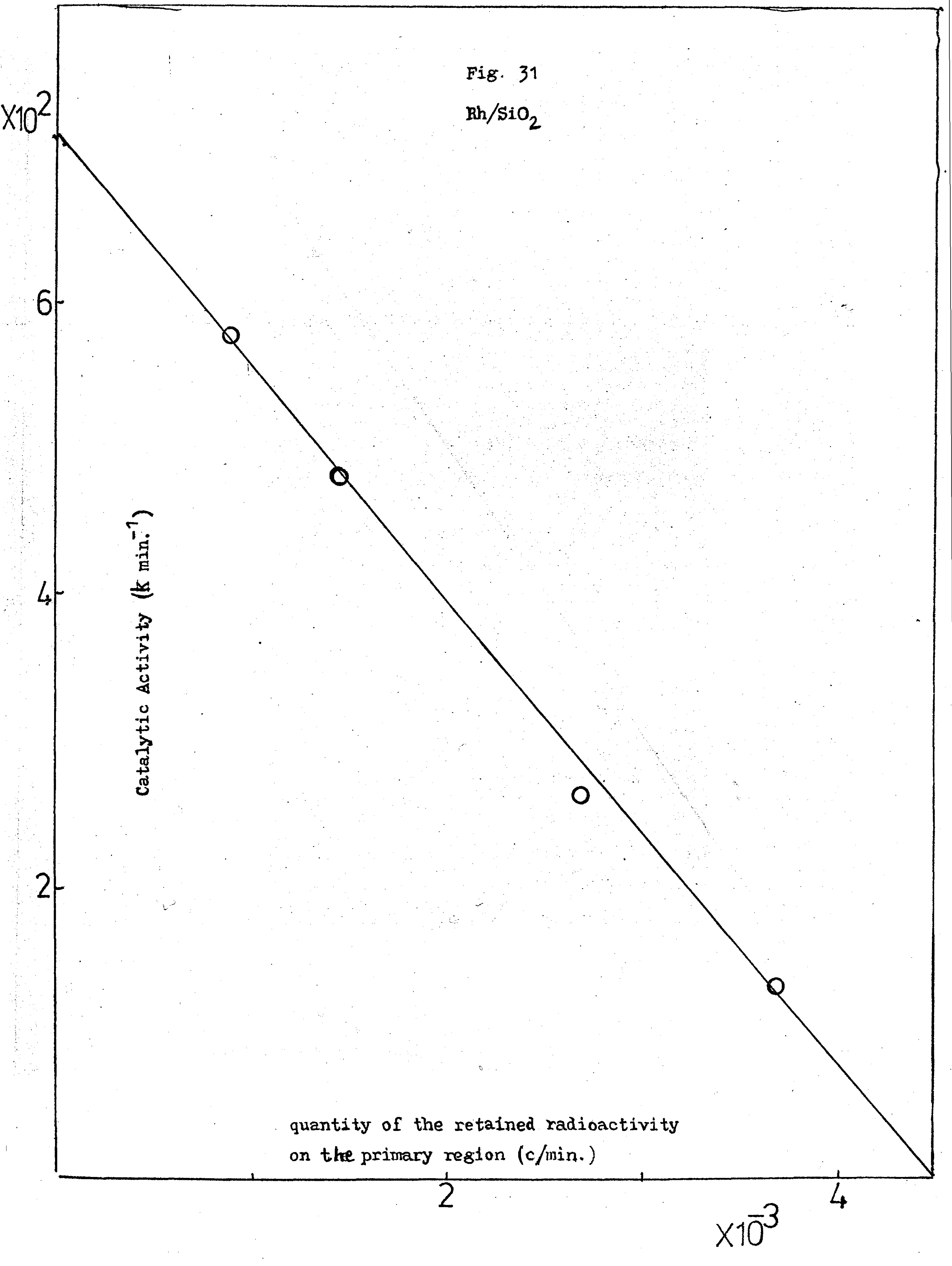


Fig. 31

Rh/SiO_2

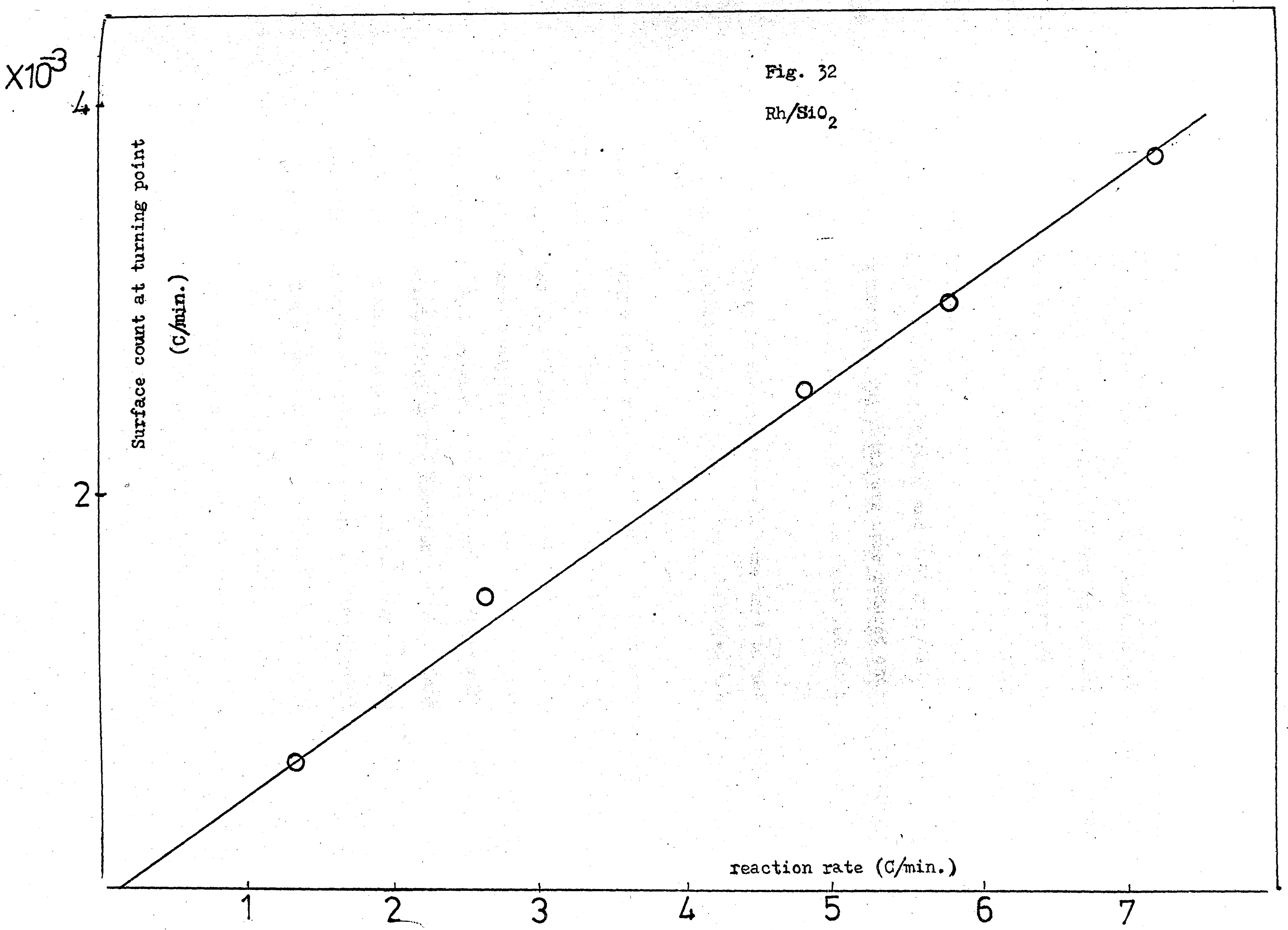


Fig. 32

Rh/SiO$_2$

3.5 ^{14}C - ethylene as a tracer in acetylene hydrogenation.

The addition of ^{14}C - ethylene to the reaction mixture of acetylene and hydrogen was used in this work to get some information about the mechanism of the hydrogenation reaction and the relative importance of the thermodynamic and the mechanistic factors in selectivity (128, 137).

0.1 g Rh/SiO_2, 0.003 g Pd/SiO_2 and 0.51 g Ir/SiO_2 was used in these experiments. The catalysts were reduced and then brought to the steady state by self poisoning as described in the previous sections.

The catalysts in the steady state were used to determine the variation of selectivity ($S = \dfrac{PC_2H_4}{PC_2H_4 + PC_2H_6}$) with respect to % conversion using a pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen. The results are shown in Tables (9 - 10) for Rh/SiO_2, Tables (20 - 23)for Pd/SiO_2 and Tables (28 - 29) for Ir/SiO_2.

To the same catalysts a pre - mixed samples containing varying pressures of ^{14}C - ethylene *, 12.5 torr acetylene and 37.5 torr hydrogen were introduced to the reaction vessel. Samples were extracted, from the reaction vessel, at different stages of the reaction, and analyzed for the amounts of ethane, ethylene and acetylene. The amounts of ^{14}C - ethane in these samples were also determined. The results after correction for the losses of material due to withdrawing samples for analysis are shown in Tables (13 - 17) for Rh/SiO_2, Tables (24 - 27) for Pd/SiO_2 and Tables (30 - 31) for Ir/SiO_2.

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* specific activity = 0.18 mCi/mM (which gives 45530 counts/ torr by the proportional counter).

The results show that ^{14}C - ethylene can be hydrogenated in the presence of acetylene to ^{14}C - ethane. However this hydrogenation takes place very slowly compared to the fast hydrogenation of ethylene in the absence of acetylene.

Figures 33(Rh/SiO_2), 36(Pd/SiO_2) and 38(Ir/SiO_2) show that the yield of ^{14}C - ethane increases linearly with % conversion up to the proximity of the acceleration point.

This linear relation between ^{14}C - ethane and % conversion indicates that the hydrogenation of ^{14}C - ethylene proceeds independently of the quantity of acetylene in the reaction vessel.

To test further the independence of ethylene hydrogenation of the quantity of acetylene the following experiments were performed:

A pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel containing 0.1 g Rh/SiO_2 catalyst in the steady state. The hydrogenation reaction was allowed to proceed up to 42% conversion at which point 5.2 torr of ^{14}C - ethylene was introduced. The quantities of ethylene, acetylene, ^{14}C - ethane and ^{12}C - ethane were determined. The same experiment was repeated with the addition of 5.2 torr ^{14}C - ethylene at 55% conversion. The results are shown in Tables 18 and 19. The plots of the quantities of ^{14}C - ethane, which were produced in these two experiments, against % conversion are straight lines with the same slope as that obtained when ^{14}C - ethylene was pre- mixed with acetylene and hydrogen before admission to the reaction vessel, (Fig. 34).

The results in Tables (13 - 17) for Rh/SiO_2, Tables (24 - 27) for Pd/SiO_2 and Tables (30 - 31) for Ir/SiO_2, show that the selectivity dropped slightly as a result of the addition of ^{14}C - ethylene.

Table 8

Self poisoning by (1:3) ^{14}C - acetylene/H_2.

amount of the retained species on the primary region (i.e. the amount of the poison counts/min)	turning point of ^{14}C - acetylene adsorption isotherm counts/min.	catalytic activity k min^{-1}
0	3740	7.16×10^{-2}
882	3000	5.77×10^{-2}
1428	2540	4.81×10^{-2}
2672	1500	2.63×10^{-2}
3683	640	1.33×10^{-2}

Table 9

Rh/SiO$_2$

% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
19.1	1.35	0.442	0.7537
26.7	1.80	0.582	0.7551
40.4	2.41	0.792	0.7528
64.8	3.45	1.13	0.7540
79.1	4.05	1.34	0.7520
90.4	4.51	1.51	0.7497

Table 10

Rh/SiO$_2$

% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
22.3	1.55	0.503	0.7551
33.0	2.09	0.683	0.7538
53.7	2.97	0.969	0.7541
73.3	3.76	1.23	0.7532
80.2	4.18	1.38	0.7515
93.3	4.61	1.56	0.7489

TABLE 13

1.04 torr ^{14}C - ethylene (0.1 gm Rh/SiO_2)

% Conversion	PC_2H_4 (torr)	PC_2H_4 (total) (torr)	^{14}C - ethane counts	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
21.1	1.47	0.789	296	0.00654	0.7504	0.7531
29.8	2.03	0.663	418	0.00924	0.7510	0.7561
35.2	2.28	0.774	494	0.0109	0.7496	0.7529
48.0	2.84	0.967	674	0.0149	0.7498	0.7551
57.1	3.2	1.05	801	0.0177	0.7509	0.7558
63.5	3.43	1.15	925	0.0204	0.7490	0.7529
77.5	3.97	1.36	1 146	0.0253	0.7506	0.7548
80.3	4.06	1.38	1 194	0.0264	0.7502	0.7521

Table 14

2.6 torr ^{14}C - ethylene (0.1gm Rh/SiO_2)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_4$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
18.9	1.35	0.462	663	0.0147	0.7453	0.7518
23.5	1.63	0.551	825	0.0182	0.7470	0.7538
36.0	2.35	0.814	1263	0.0279	0.7436	0.7562
42.6	2.64	0.906	1495	0.0330	0.7451	0.7520
58.0	3.24	1.10	2036	0.0450	0.7471	0.7551
64.2	3.45	1.20	2330	0.0515	0.7439	0.7528
73.5	3.83	1.34	2726	0.0602	0.7418	0.7527

Table 15

5.2 torr ^{14}C - ethylene (0.1gm Rh/SiO$_2$)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
4.0	0.257	0.105	681	0.0150	0.7101	0.7512
16.0	1.15	0.411	1496	0.0329	0.7370	0.7529
21.1	1.45	0.509	1703	0.0374	0.7401	0.7552
30.2	1.96	0.683	2274	0.0500	0.7415	0.7556
42.0	2.5	0.875	3191	0.0701	0.7410	0.7570
51.9	2.95	1.04	3788	0.0833	0.7390	0.7551
64.8	3.40	1.23	4754	0.105	0.7349	0.7524
80.1	3.97	1.48	6031	0.133	0.7280	0.7463
93.2	4.38	1.67	7206	0.158	0.7240	0.7442

Table 16

5.2 torr ^{14}C - ethylene (0.1gm Rh/SiO$_2$)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
17.3	1.23	0.427	1265	0.0278	0.7422	0.7549
30.1	2.02	0.706	2250	0.0495	0.7410	0.7549
50.6	2.87	0.997	3380	0.0743	0.7423	0.7568
61.3	3.27	1.19	4347	0.0955	0.7332	0.7495
74.2	3.85	1.42	5635	0.124	0.7312	0.749
90.1	4.28	1.63	6807	0.150	0.7246	0.744

Table 17

10.4 torr ^{14}C - ethylene (0.1gm Rh/SiO$_2$)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
22.0	1.55	0.585	3088	0.0682	0.726	0.7518
31.5	2.09	0.772	4422	0.0977	0.730	0.7561
44.1	2.67	1.022	6190	0.137	0.727	0.7526

TABLE 18

01gm Rh/SiO_2 12.5 torr C_2H_2 + 37.5 torr H_2

BEFORE THE ADDITION OF $^{14}C_2H_4$

% conversion	PC_2H_2	PC_2H_4	PC_2H_6	selectivity (S)
24.2	9.1	1.651	0.5384	0.7541
42.4	6.42	2.493	0.8147	0.7537

AFTER THE ADDITION OF 5.2 TORR ^{14}C – ETHYLENE

% conversion	PC_2H_2	PC_2H_4	PC_2H_6 (Total)	$^{14}C_2H_4$ (Count)	$^{14}PC_2H_6$	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$ (Total)
54.1	5.25	3.011	0.996	903	0.01998	0.7513
65.4	4.22	3.455	1.163	1708	0.0378	0.7482
71.5	3.73	3.693	1.257	2312	0.05116	0.746
85.1	2.75	4.25	1.471	3396	0.07514	0.7429

Table 19

0.1 gm Rh/SiO$_2$ 12.5 torr C_2H_2 + 37.5 torr H_2

before the addition of $^{14}C_2H_4$:

% conversion	PC_2H_2	PC_2H_4	PC_2H_6	selectivity (S)
20.6	9.71	1.448	0.4734	0.7536
34.3	7.48	2.153	0.6981	0.7552
42.1	6.52	2.511	0.8201	0.7538
55.6	5.03	3.053	0.9960	0.754

After the addition of $^{14}C_2H_4$

% conv	PC_2H_2	PC_2H_4	PC_2H_6 (total)	$^{14}C_2H_6$ (counts)	$P^{14}C_2H_6$	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6\ (\text{total})}$
60.5	4.59	3.249	1.0687	350	0.00774	0.7525
66.6	4.08	3.498	1.1582	775	0.0172	0.7513
69,9	3.84	3.647	1.219	1076	0.0238	0.7495
75.8	3.37	3.845	1.301	1594	0.0353	0.7471
82.8	2.88	4.153	1.424	2230	0.0493	0.7446

Table 20

0.003 gm Pd/SiO_2

Exp. 1	% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
	16.1	1.59	0.101	0.9403
	37.9	3.53	0.223	0.9405
	48.2	4.41	0.277	0.941
	57.3	5.05	0.319	0.9406
	65.6	5.80	0.372	0.9377
	75.4	6.59	0.415	0.9407
	86.5	7.70	0.493	0.9398

Table 21

0.003 gm Pd/SiO_2

Exp. 2	% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
	13.0	1.50	0.095	0.9408
	22.5	2.15	0.114	0.9405
	37.2	3.40	0.212	0.941
	51.1	4.68	0.297	0.9403
	67.5	5.97	0.377	0.9406
	80.1	7.03	0.454	0.9394

Table 22

0.003 gm Pd/SiO_2

Exp. 3	% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
	17.0	1.7	0.110	0.9393
	31.3	2.90	0.186	0.9398
	41.5	3.71	0.233	0.9408
	56.1	4.93	0.314	0.9402
	73.4	6.51	0.417	0.9398
	80.0	7.10	0.449	0.9406

Table 23

0.003 gm Pd/SiO_2

Exp. 4	% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
	20.6	2.00	0.127	0.9402
	31.4	2.89	0.181	0.941
	49.7	4.50	0.270	0.9395
	55.9	4.99	0.325	0.939
	61.6	5.50	0.352	0.9400
	89.6	7.87	0.510	0.9390

Table 24

5.1 torr ^{14}C - ethylene (0.003 gm Pd/SiO$_2$)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$PC_2^{14}H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4+PC_2H_6-PC_2^{14}H_6}$
18.6	1.34	0.098	647	0.0142	0.9318	0.9411
22.5	2.61	0.186	785	0.0173	0.9335	0.9393
33.1	2.80	0.186	1100	0.0242	0.9322	0.9407
51.4	3.77	0.274	1718	0.0378	0.9321	0.9409
60.7	6.75	0.448	2061	0.0454	0.934	0.9400
77.3	7.00	0.475	2729	0.060	0.9327	0.9407
88.4	7.3	0.544	3117	0.0686	0.9307	0.9390

Table 25

5.0 torr ^{14}C - ethylene (0.003 gm Pd/SiO_2)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4+PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4+PC_2H_6-P^{14}C_2H_6}$
20.5	1.95	0.140	697	0.0153	0.9331	0.9400
44.1	3.54	0.256	1524	0.0335	0.9326	0.9409
68.2	5.02	0.367	2291	0.0504	0.9319	0.9407
81.6	7.40	0.492	2889	0.0636	0.9316	0.9399
87.3	7.51	0.554	3120	0.0687	0.9313	0.9393

Table 26

2.5 torr ^{14}C - ethylene (0.003gm Pd/SiO_2)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4+PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4+PC_2H_6-P^{14}C_2H_6}$
21.5	2.43	0.162	375	0.0083	0.9374	0.9405
27.2	3.00	0.208	450	0.0099	0.9354	0.9398
36.3	3.88	0.264	602	0.0133	0.9363	0.9393
47.6	5.55	0.368	829	0.0183	0.9378	0.9407
66.9	5.96	0.400	1136	0.025	0.9372	0.9409
75.4	6.30	0.431	1260	0.028	0.9360	0.9402
86.7	7.43	0.511	1518	0.033	0.9356	0.9401

Table 27

10.3 torr ^{14}C - ethylene (0.003 gm Pd/SiO_2)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
17.0	1.62	0.129	1125	0.0248	0.9261	0.9394
28.1	2.88	0.228	1940	0.0427	0.9267	0.9396
39.5	3.08	0.253	2691	0.0592	0.9242	0.9409
51.2	4.47	0.360	3455	0.0761	0.9256	0.9404
67.8	5.50	0.450	4655	0.1025	0.9244	0.9406
79.3	7.36	0.598	5543	0.122	0.9248	0.9392
87.5	7.67	0.638	6269	0.138	0.9231	0.9387

Table 28

0.51 g Ir/SiO$_2$

Exp. 1	% conversion	PC$_2$H$_4$ (torr)	PC$_2$H$_6$ (torr)	selectivity
	20.3	0.35	1.79	0.1635
	36.9	0.59	3.04	0.1625
	52.1	0.81	4.19	0.1620
	59.0	1.01	5.17	0.1634
	73.5	1.22	6.28	0.1626
	90.3	1.50	7.82	0.1610

Table 29

0.51 g . Ir/SiO$_2$

Exp. 2	% conversion	PC$_2$H$_4$ (torr)	PC$_2$H$_6$ (torr)	selectivity
	25.1	0.41	2.10	0.1633
	33.5	0.52	2.68	0.1625
	39.7	0.70	3.58	0.1636
	62.8	1.01	5.23	0.1619
	80.6	1.32	6.82	0.1621
	88.2	1.49	7.75	0.1613

Table 30

2.5 torr ^{14}C - ethylene (0.51 gm Ir/SiO_2)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
19.5	0.30	1.56	1103	0.0243	0.1613	0.1630
29.6	0.49	2.54	1406	0.0310	0.1617	0.1633
41.8	0.65	3.40	2252	0.0497	0.1605	0.1625
55.4	0.93	4.83	2798	0.0618	0.1615	0.1632
90.9	1.50	7.92	5177	0.114	0.1592	0.1611

Table 31

5.1 torr ^{14}C - ethylene (0.51gm Ir/SiO_2)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
23.1	0.38	2.00	2396	0.053	0.1597	0.1631
38.6	0.61	3.24	4188	0.092	0.1585	0.1622
50.6	0.86	4.52	5231	0.115	0.1599	0.1635
63.2	1.03	5.46	6673	0.147	0.1587	0.1625
81.2	1.37	7.3	9011	0.199	0.1580	0.1617
88.7	1.45	7.74	9896	0.218	0.1578	0.1616

Figures 35 (Rh/SiO_2), 37 (Pd/SiO_2) show that the quantity of ^{14}C - ethane is directly proportional to the pressure of ^{14}C - ethylene added to the reaction mixture.

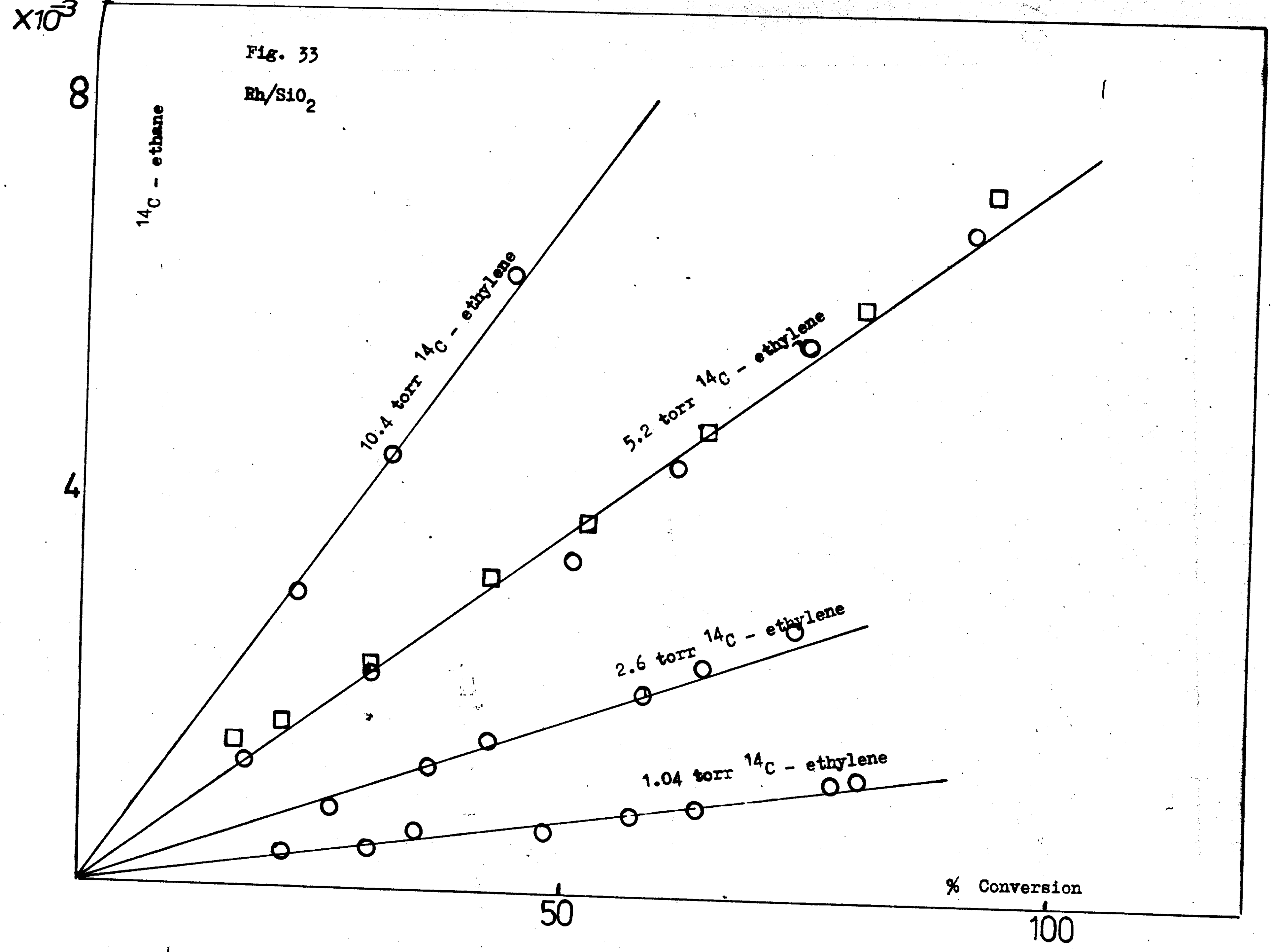
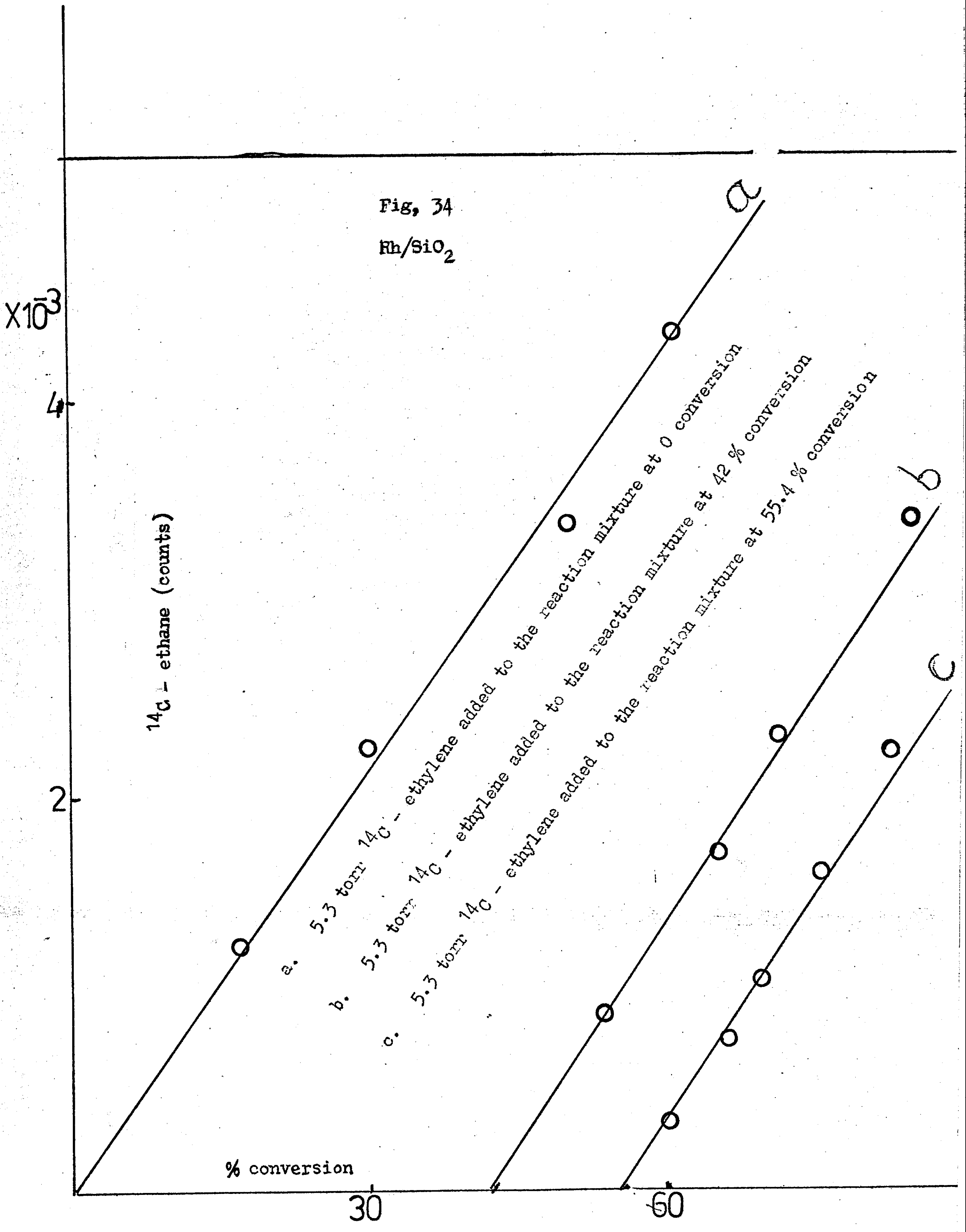


Fig. 33

Rh/SiO$_2$



Fig, 34

Rh/SiO$_2$

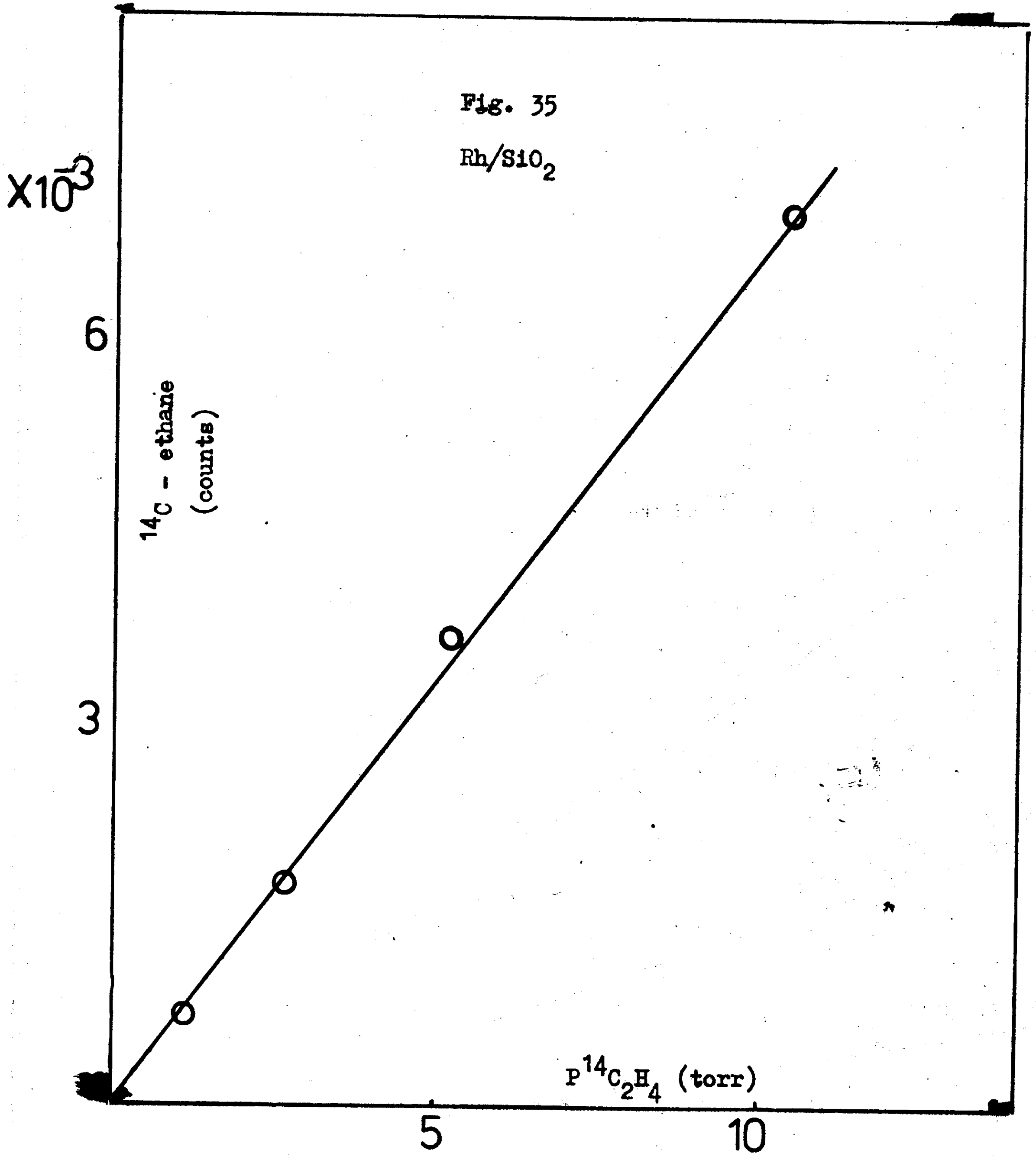


Fig. 35
Rh/SiO$_2$
X10^{-3}
6
3
^{14}C - ethane (counts)
P^{14}C$_2$H$_4$ (torr)
5
10

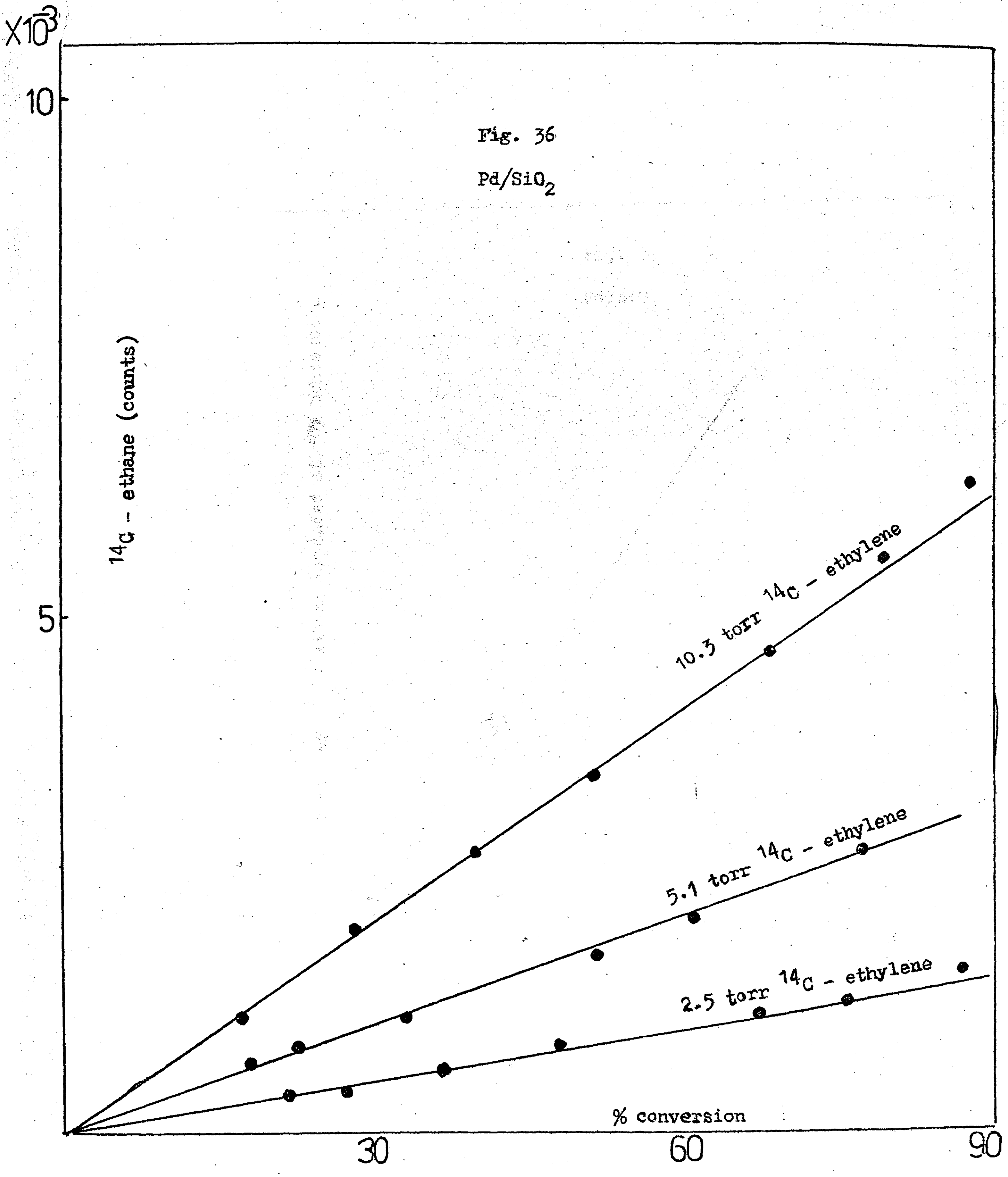


Fig. 36

Pd/SiO$_2$

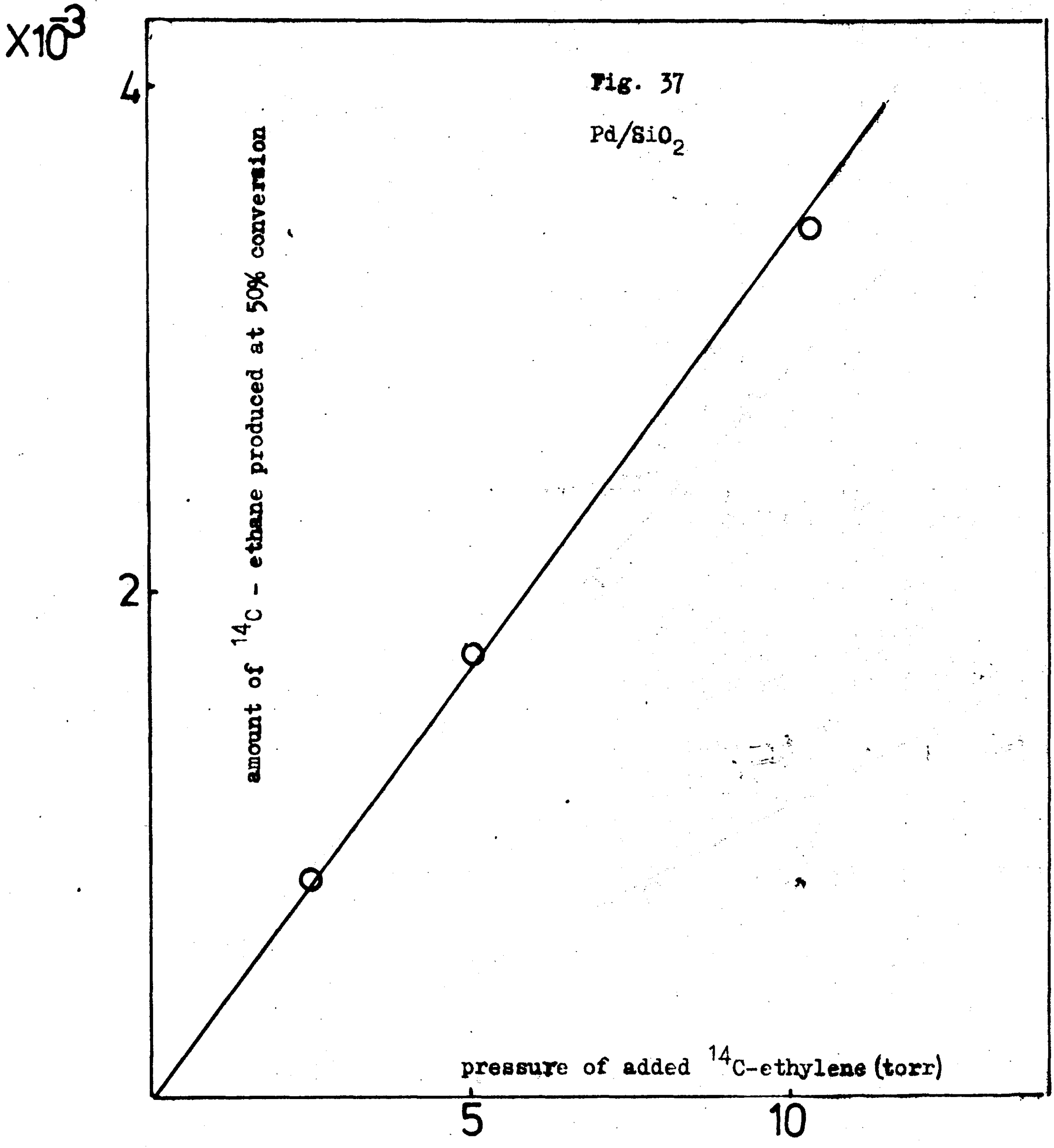


Fig. 37

X10⁻³
4
2
Pd/SiO₂
amount of ¹⁴C - ethane produced at 50% conversion
pressure of added ¹⁴C-ethylene (torr)
5
10

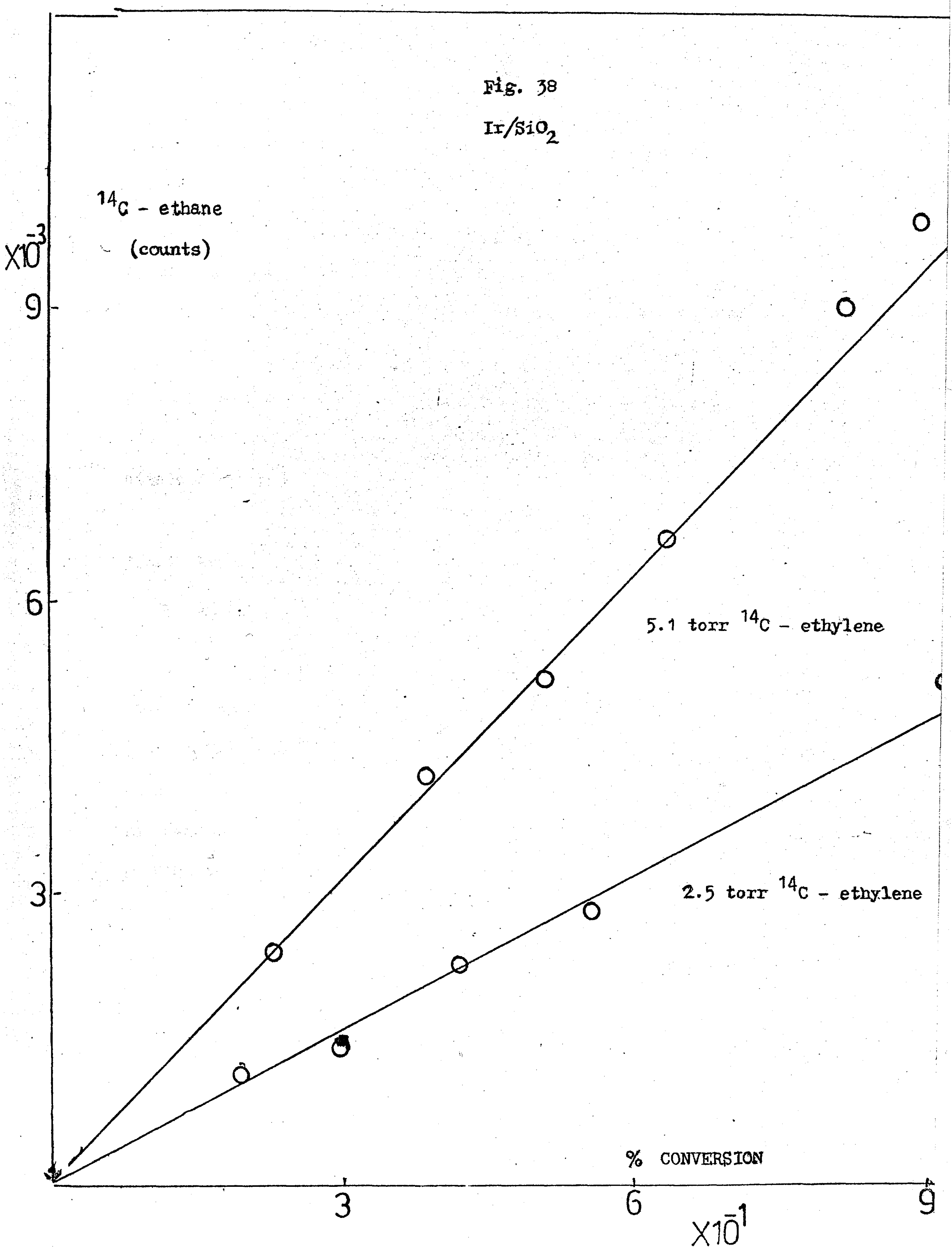


Fig. 38
Ir/SiO$_2$
^{14}C - ethane
(counts)
X10^{-3}
9
6
3
5.1 torr ^{14}C - ethylene
2.5 torr ^{14}C - ethylene
% CONVERSION
3
6
9
X10^{-1}

3.6 Behaviour of ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms on catalysts in their steady states.

The results in section 3.2 show that the adsorbed species which give rise to the reaction products is adsorbed on the secondary adsorption isotherm. For this reason it was decided to perform a set of experiments by which the behaviour of these species can be studied.

The following experiments were performed using catalyst in their steady states in order to eliminate the interference of the primary region, which disappeared completely (except for Pd/SiO_2 ^{14}C - acetylene adsorption isotherm) when the steady state was attained by self poisoning.

3.6.1 Effect of evacuation on ^{14}C - ethylene secondary adsorption isotherm on catalysts in their steady state.

0.3 g Rh/SiO_2 was used. The catalyst was brought to the steady state by self poisoning. The deactivated catalyst was evacuated for one hr; the ^{14}C - ethylene adsorption isotherm was build on this deactivated catalyst and the effect of evacuation was studied. The same experiments were performed using 0.1 g Pd/SiO_2 and 0.51 g Ir/SiO_2 in their steady states. The results, which are shown in Tables (32 - 34), show that, with all the catalysts, only a small amount of the surface ^{14}C - ethylene can be removed by evacuation. The amount removed cannot be increased by increasing the time of evacuation.

TABLES 32, 33, 34

Variation of (^{14}C) Acetylene and (^{14}C) Ethylene Surface Count Rates with Various Treatments at 298K.

	Catalyst	Adsorbate	Gas Pressure (torr)	Surface Count Rate (min^{-1})					
				Initial	Evacuation	C_2H_2	C_2H_4	H_2	H_2+ C_2H_2
Table 32	Rh/SiO_2 (0.30g)	C_2H_4	1.98	2225	2179	2195		-	1060
			3.14	3518	3457	3463	3518	-	1818
			6.50	7117	7090	7082	-	-	3557
	Rh/SiO_2 (0.10g)	$C_2H_4^*$	0.51	820	782	-	-	710	-
	Rh/SiO_2 (0.30g)	C_2H_2	1.12	1248	1212	1248	1248	-	-
			2.08	2322	2267	2320	-	2176	-
			4.04	4513	4369	4513	4513	4370	-
			5.07	5655	5508	5655	-	5513	-
Table 33	Pd/SiO_2 (0.10g)	C_2H_4	0.62	482	482	481	-	-	115
			3.77	2887	2823	2799	2887	-	2212
			6.46	4943	4921	4841	-	-	3843
	Pd/SiO_2 (0.10g)	C_2H_2	1.37	5112	5009	5112	5112	3760	-
			3.77	10350	10173	10350	10350	9023	-

	Pd/Al_2O_3	C_2H_4	0.63	150	150	-	-	-	25
	(0.10g)		0.67	180	178	82	180	-	-
	Pd/Al_2O_3	C_2H_2	0.59	1546	1528	-	1545	-	-
	(0.10g)		0.61	1612	1600	1612	-	1187	-
			0.46	2135	2112	1667	2135	-	875
Table 34	Ir/SiO_2	C_2H_4	0.71	3313	3267	2831	3313	-	1363
	(0.51g)		2.00	9315	9298	9156	9315	-	3838
	Ir/SiO_2	C_2H_2	0.31	1835	1794	1835	1835	1315	-
	(0.51g)		0.59	3350	3297	3350	3350	50	-

(^{14}C) specific activities: 0.025mCi/mmol (Rh), or 0.10mCi/mmol (Rh*); 0.05mCi/mmol (Pd) and 0.10mCi/mmol (Ir).

3.6.2 Effect of evacuation on ^{14}C - acetylene secondary adsorption isotherm on catalyst in their steady states.

The same catalysts, which were used in section 3.6.1. were used here. The catalysts were kept, before each new experiment, under 80 torr hydrogen at room temperature either overnight or at least for 4 hr. to remove most of the surface adsorbed species from the previous experiment. The catalyst was then evacuated for one hr. ^{14}C - acetylene adsorption isotherm was build up and the effect of evacuation on the adsorbed species was studied.

Tables (32 - 34) show that only a small amount of surface ^{14}C - acetylene can be removed by evacuation, and the amount removed cannot be increased by increasing the time of evacuation.

3.6.3 Molecular exchange of ^{14}C - ethylene species adsorbed on the secondary adsorption isotherm using catalysts in their steady states.

After building up the ^{14}C - ethylene secondary adsorption isotherm the catalysts were evacuated for one hr. 12 torr of ethylene was introduced to the reaction vessel. The surface and gas phase radioactivities were determined. The results for all the catalysts (Rh/SiO_2, Ir/SiO_2 and Pd/SiO_2) indicate that no molecular exchange has taken place.

3.6.4 Molecular exchange of ^{14}C - acetylene species adsorbed on ^{14}C - acetylene adsorption isotherm using catalysts in their steady states.

After building up the ^{14}C - acetylene adsorption isotherm the catalyst was evacuated for one hr. 12.5 torr acetylene were introduced to the reaction vessel. The surface and gas phase radioactivities were determined. The results for all the catalysts (Rh/SiO_2, Ir/SiO_2, Pd/SiO_2) indicate that no molecular exchange takes place.

3.6.5 ^{14}C - ethylene secondary adsorption isotherm on acetylene precovered surface.

The catalysts in their steady states were covered with 12.5 torr non-radioactive acetylene, then, without removing the acetylene from the gas phase, ^{14}C - ethylene secondary adsorption isotherms were built. Figure (39) shows that in the case of Rh/SiO_2 the slope of ^{14}C - ethylene secondary adsorption was decreased by 30% by the presence of 12.5 torr acetylene in the gas phase.

Figures 40 (Pd/SiO_2) and 41 (Ir/SiO_2) show that the extent of ^{14}C - ethylene adsorption is nearly <u>independent</u> of the presence or absence of acetylene in the gas phase.

3.6.6 Effect of hydrogen on ^{14}C - acetylene adsorption isotherm using catalysts in their steady states.

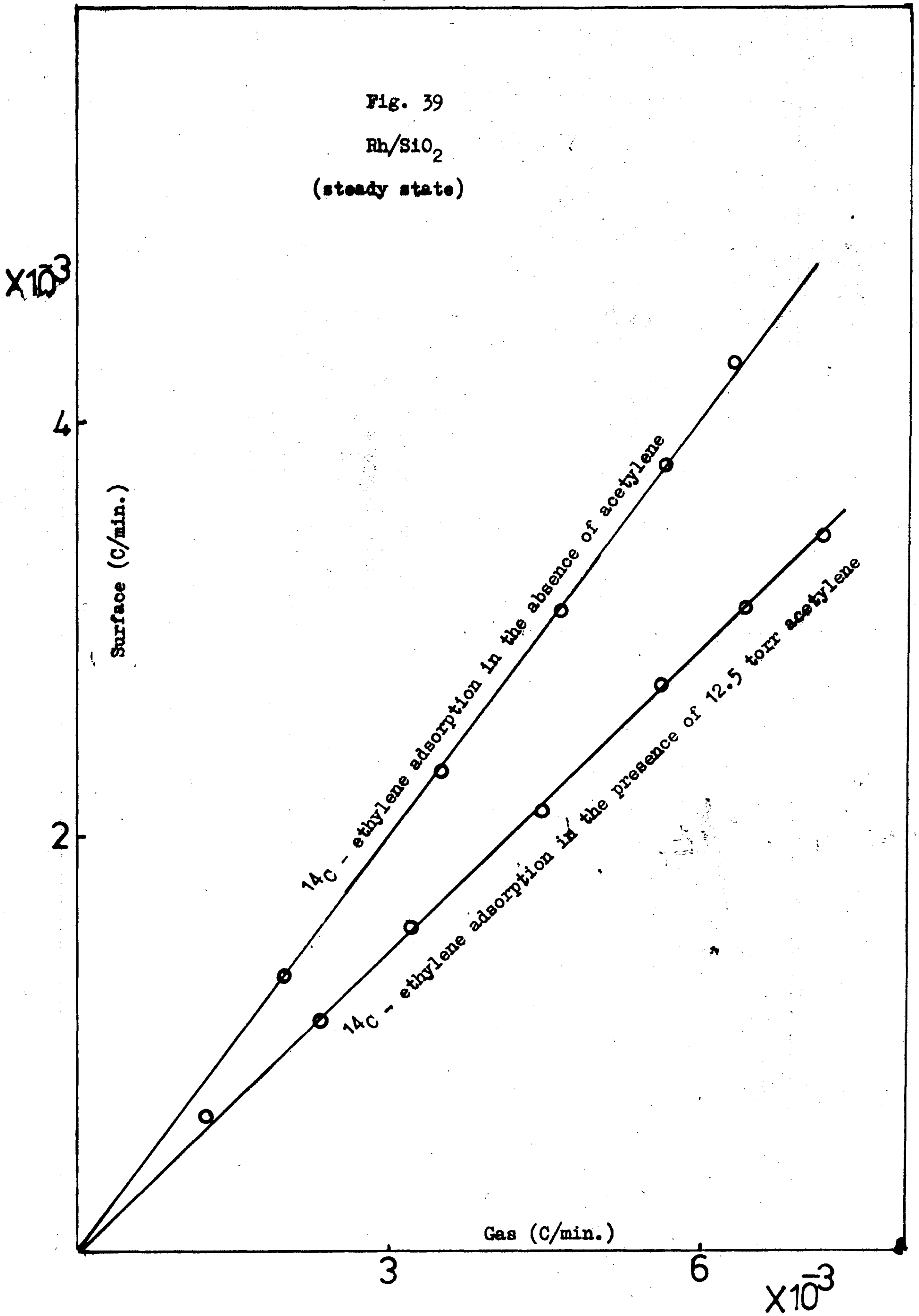
^{14}C - acetylene adsorption isotherms were build up on the catalysts (Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2) in their steady states. The reaction vessel was evacuated for one hr to remove the gas phase ^{14}C - acetylene. 37.5 torr hydrogen was introduced to the reaction vessel. The drop in the surface radioactivity was measured. These experiments were repeated with a varying amount of the adsorbed species on the secondary adsorption isotherm.

Before performing any new experiment the catalyst from the previous experiment was kept under 37.5 torr hydrogen at room

Fig. 39

Rh/SiO_2

(steady state)



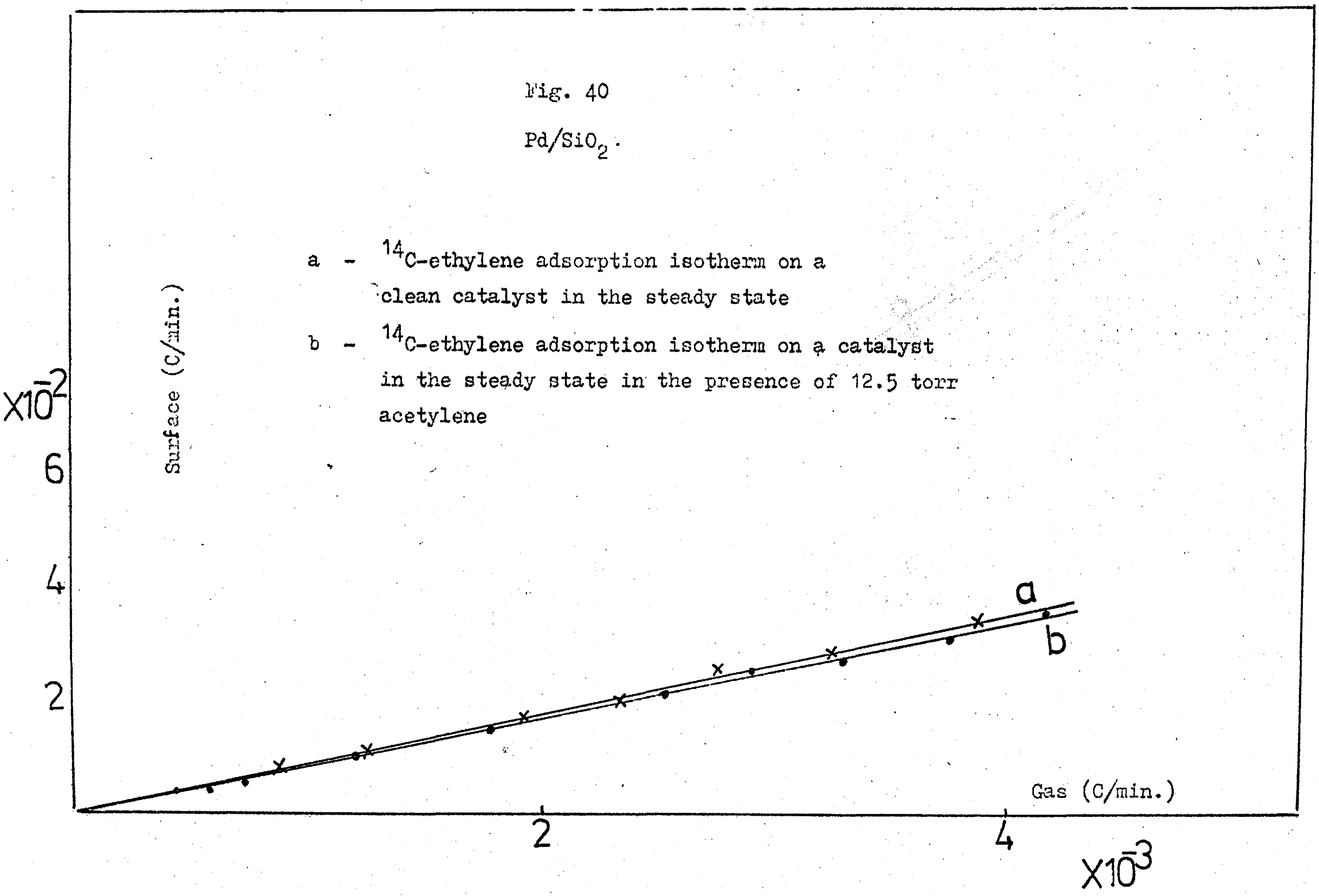


Fig. 40

Pd/SiO_2.

a - ^{14}C-ethylene adsorption isotherm on a clean catalyst in the steady state

b - ^{14}C-ethylene adsorption isotherm on a catalyst in the steady state in the presence of 12.5 torr acetylene

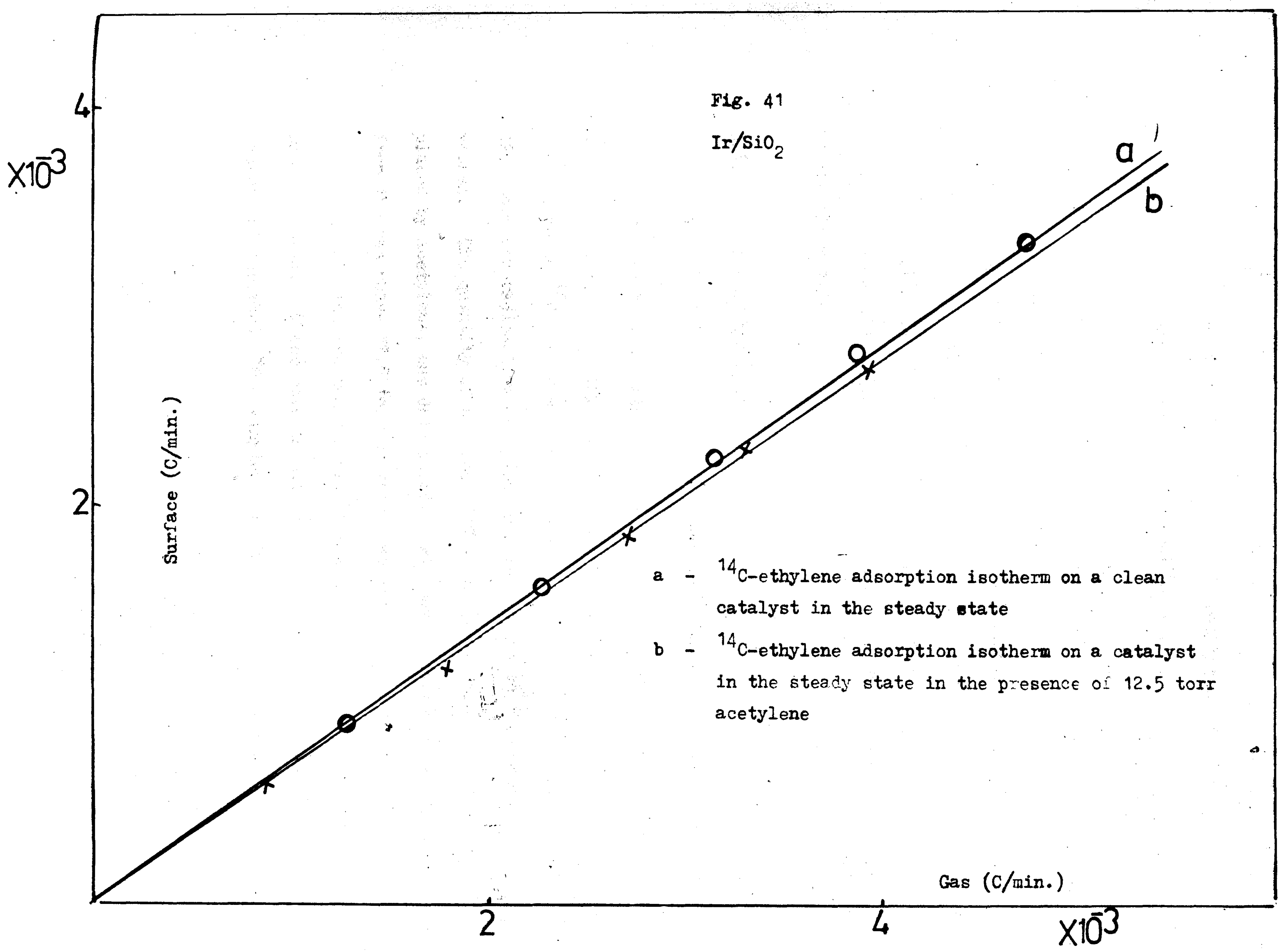


Fig. 41

Ir/SiO$_2$

a – ^{14}C-ethylene adsorption isotherm on a clean catalyst in the steady state

b – ^{14}C-ethylene adsorption isotherm on a catalyst in the steady state in the presence of 12.5 torr acetylene temperature for a sufficient period to remove most of the adsorbed species.

The results show that, for Rh, Ir and Pd catalysts, the removal of ^{14}C - acetylene adsorbed species takes place in two distinct stages; a very fast removal during the first stage followed by a very slow removal during the second stage. In some experiments, when the quantity of the adsorbed species was large, the slow removal during the second stage was completed only after the catalyst had been kept under 37.5 torr hydrogen for 48 hr.

Figures (42, 43, 44) show typical graphs of the behaviour of the adsorbed species under hydrogen. The results are shown in Tables (32 - 34).

3.6.7 Effect of hydrogen and acetylene on ^{14}C - ethylene secondary adsorption using catalysts in their steady states.

The catalyst in the steady state was evacuated for one hr before building ^{14}C - ethylene secondary adsorption isotherm. The gas phase ^{14}C - ethylene was removed by one hr evacuation. 12.5 torr non-radioactive acetylene was introduced to the reaction vessel. The quantity of adsorbed ^{14}C - ethylene, which was displaced by acetylene, was determined. Without removing the acetylene from the gas phase 37.5 torr hydrogen was introduced to the reaction vessel, and the removal of ^{14}C - ethylene by C_2H_2/H_2 mixture was monitored. These experiments were repeated with varying amounts of adsorbed ^{14}C - ethylene on the secondary adsorption region.

Before performing any further experiments the catalyst from the previous experiment was kept at room temperature under 37.5 torr

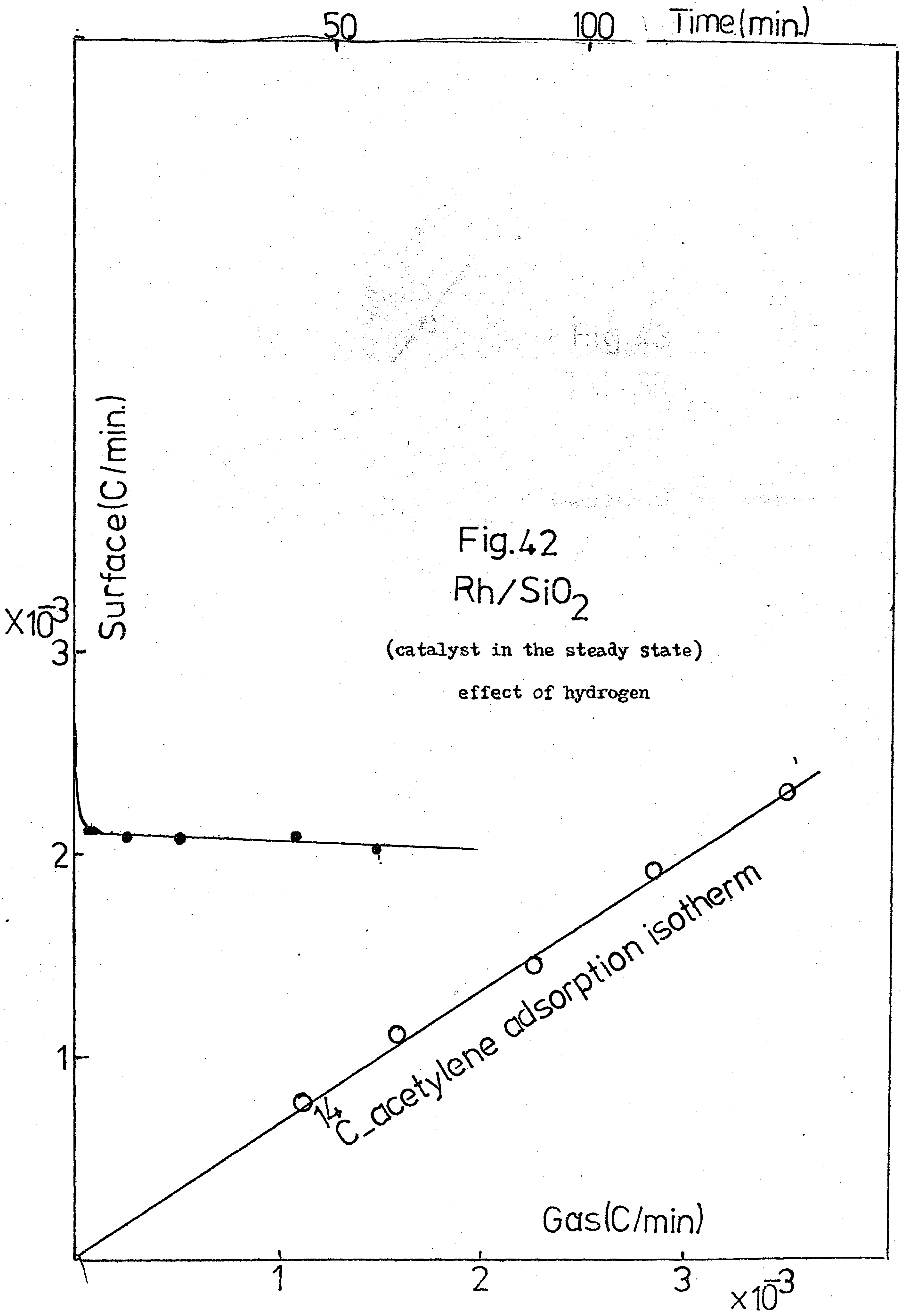


Fig. 42

Rh/SiO_2

(catalyst in the steady state)

effect of hydrogen

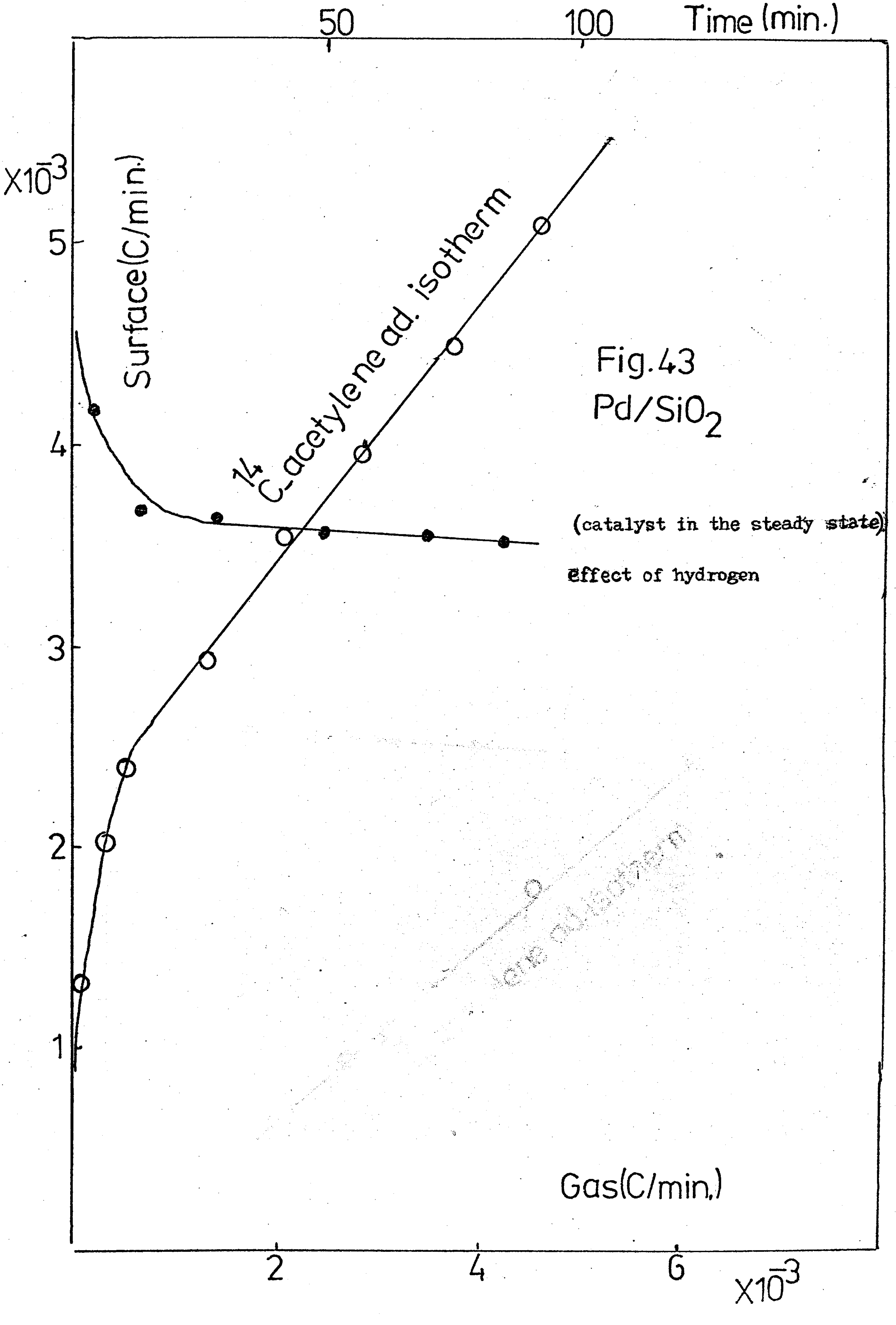


Fig. 43 Pd/SiO$_2$

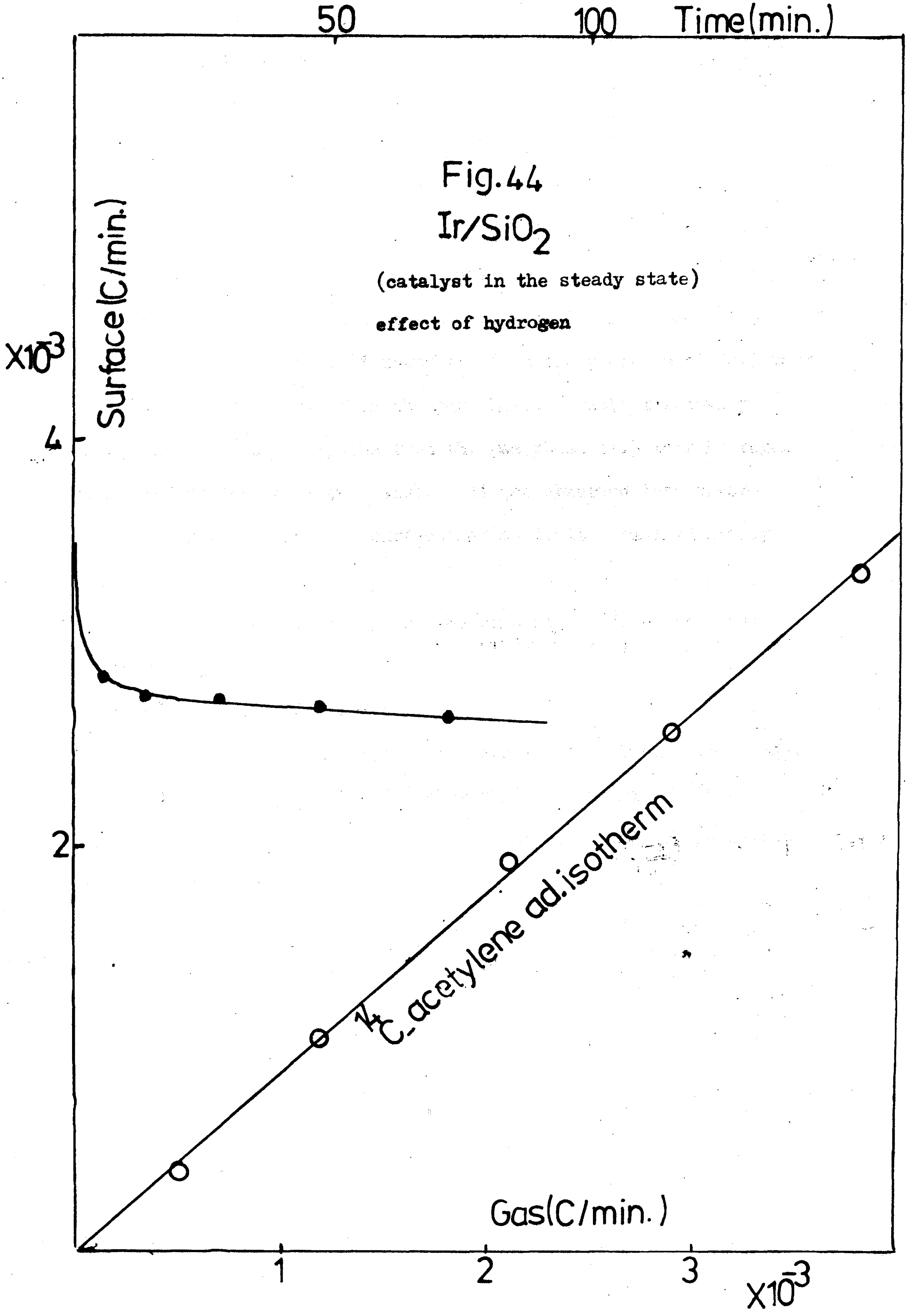


Fig.44

Ir/SiO_2

(catalyst in the steady state)

effect of hydrogen

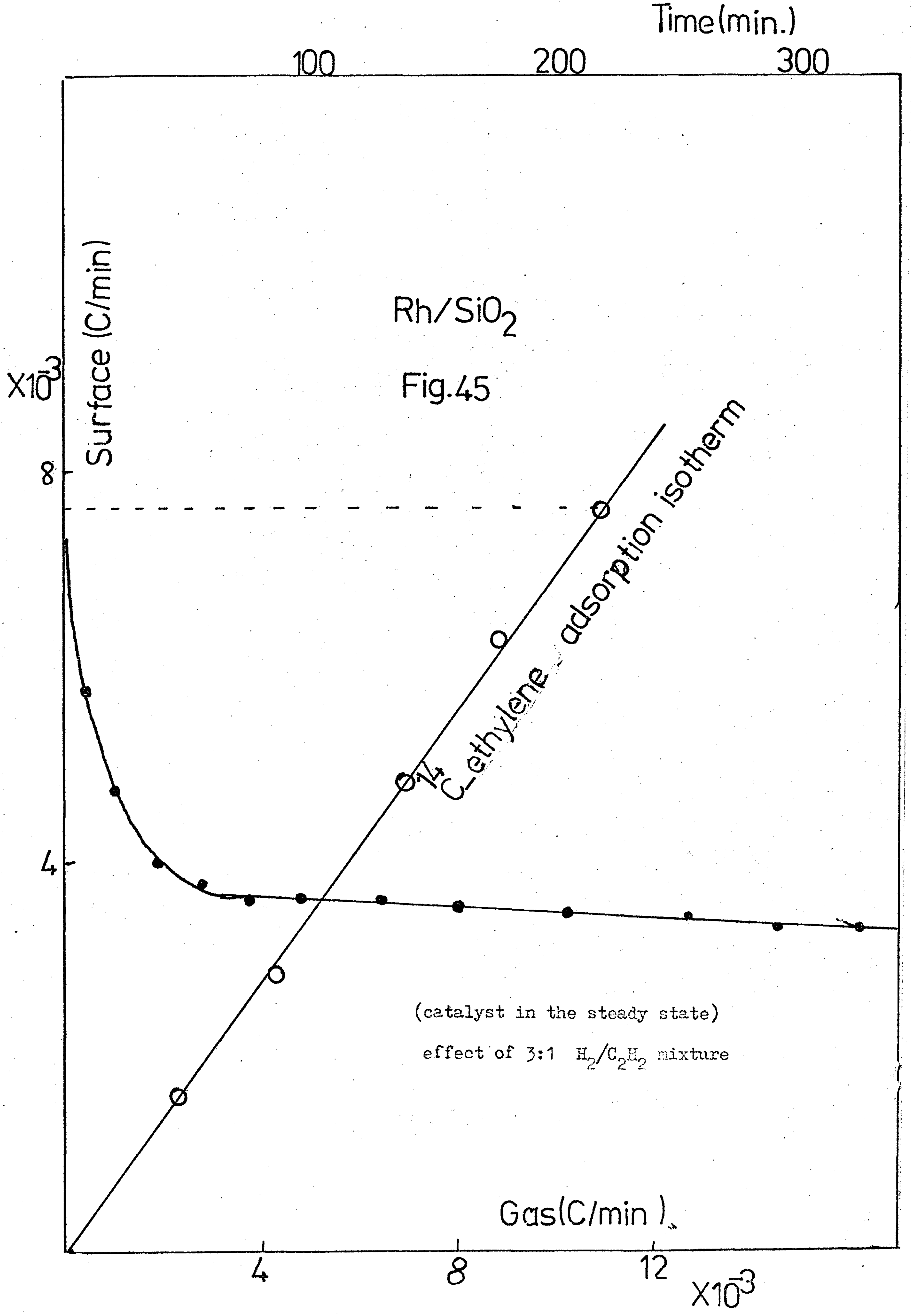
hydrogen for a sufficient time to remove most of the adsorbed species. The results of these experiments are shown in Tables (32 - 34).

These experiments show that the removal of ^{14}C - ethylene by H_2/C_2H_2 mixture takes place in two distinct stages; fast removal, followed by a very slow removal (Figures 45, 46, 47). The results of these experiments are shown in Tables (32 - 34).

Another set of experiments was performed in which the ^{14}C - ethylene secondary adsorption was build in the presence of 12.5 torr non-radioactive acetylene in the gas phase. Without removing acetylene and ^{14}C - ethylene from the gas phase 37.5 torr hydrogen was added to the reaction vessel. It was observed that before the acceleration point the surface radioactivity remained nearly constant.

After the acceleration point the removal of ^{14}C - ethylene in these experiments takes place in two stages; a fast removal followed by a very slow removal.

The results of these experiments are shown in Tables (32 - 34). The results in Tables (32 - 34) show that the amount of ^{14}C - ethylene removed by H_2/C_2H_2 mixture is proportional to the extent of the secondary region.



Rh/SiO_2

Fig.45

(catalyst in the steady state)

effect of 3:1 H_2/C_2H_2 mixture

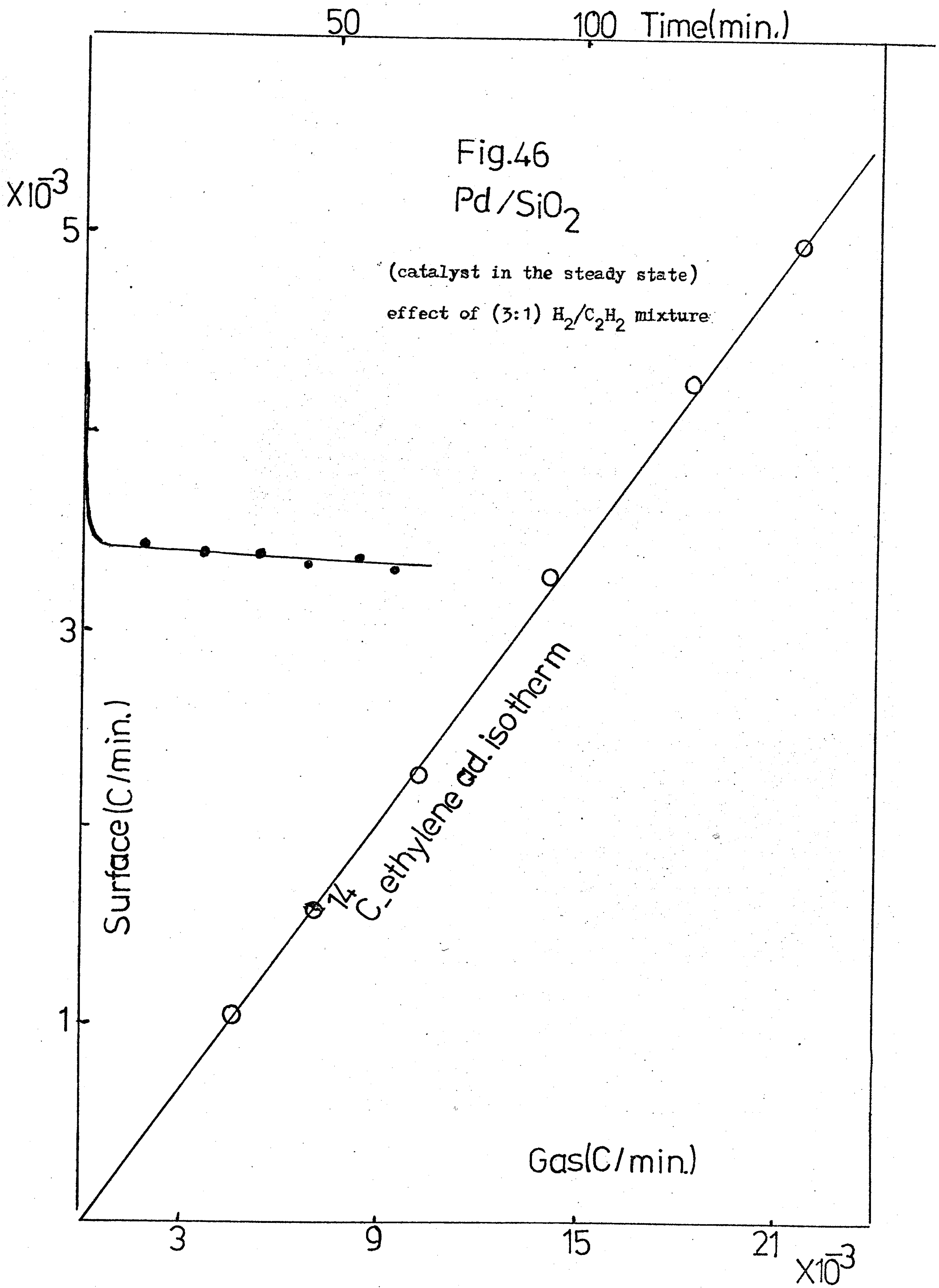


Fig.46

Pd/SiO_2

(catalyst in the steady state)

effect of (3:1) H_2/C_2H_2 mixture

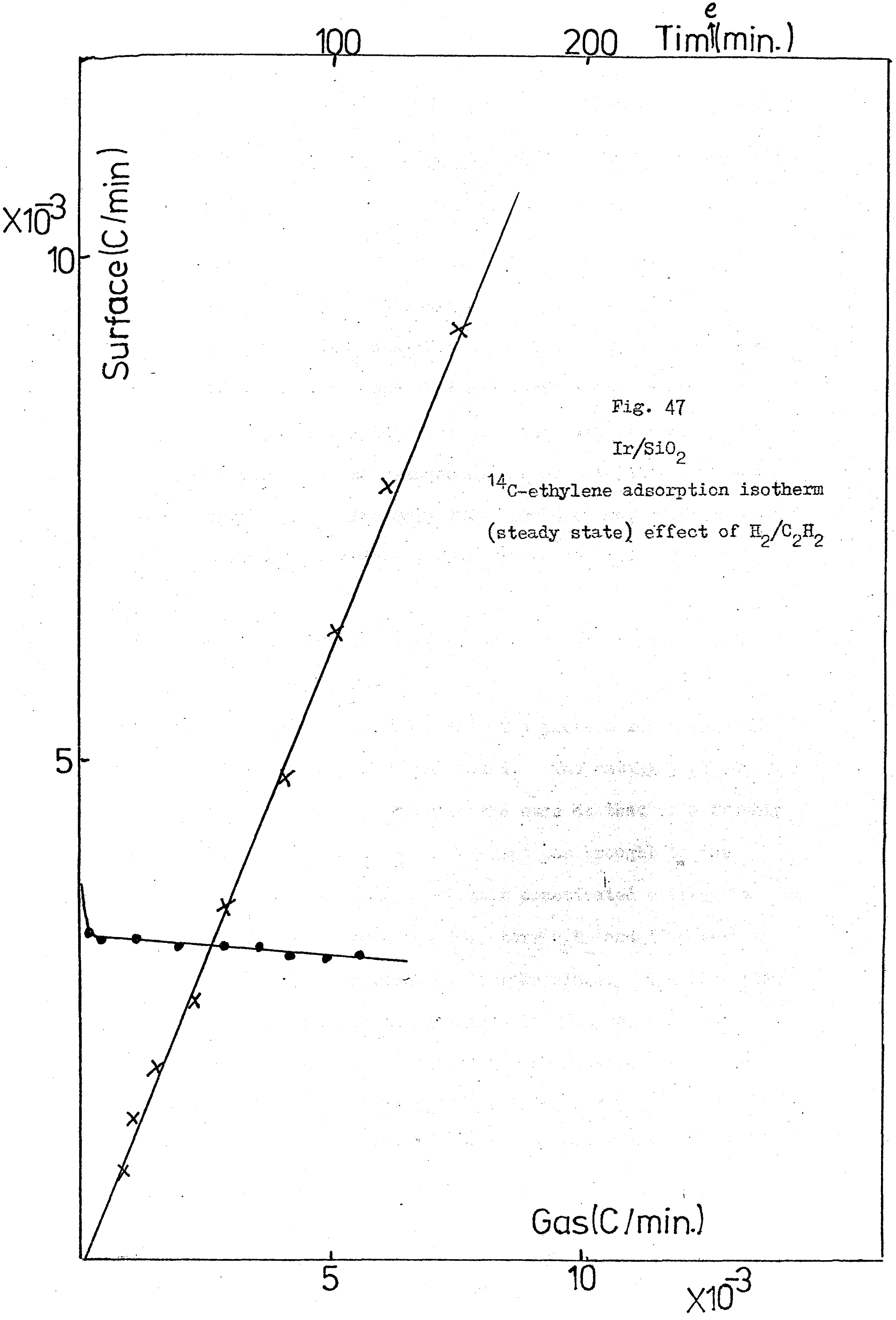


Fig. 47

Ir/SiO$_2$

^{14}C-ethylene adsorption isotherm

(steady state) effect of H_2/C_2H_2

3.7 Poisoning of acetylene hydrogenation by carbon monoxide.

3.7.1 Poisoning of acetylene hydrogenation by CO using Rh/SiO_2 catalyst.

0.2 gm Rh/SiO_2 was reduced and then allowed to cool down to ambient temperature before evacuation. A pre - mixed sample of one torr CO, 12.5 torr C_2H_2 and 37.5 torr H_2 was introduced to the reaction vessel. It was found that no reaction took place although the reaction mixture was kept over the catalyst for 12 hr.

The reaction mixture was removed by one hr evacuation, then a pre - mixed sample containing only 12.5 torr C_2H_2 and 37.5 torr H_2 was introduced to the reaction vessel; no reaction was observed to take place.

The poisoned catalyst was cleaned by a stream of hydrogen for 4 hr at 623 K, then allowed to cool to ambient temperature before evacuation. To this prereduced catalyst a pre - mixed sample of 12.5 torr C_2H_2 and 37.5 torr H_2 was added. The catalyst shows very high catalytic activity which is the same as that of a freshly reduced catalyst. The prereduced catalyst was brought to the steady state by self poisoning. To this deactivated catalyst a pre - mixed sample of one torr CO, 12.5 torr C_2H_2 and 37.5 torr H_2 was added; no reaction was observed to take place. The catalytic activity of this poisoned catalyst cannot be restored by evacuating the reaction vessel for one hr, but it can be restored by cleaning the catalyst by a stream of H_2 for 4 hr at 623 K.

It was decided to study the mechanism of CO poisoning from the effect of the experimental variables on ^{14}C - CO adsorption isotherm.

3.7.1.1 ^{14}C - CO adsorption isotherm on a freshly reduced, clean Rh/SiO_2 surface.

The catalyst which was used in section 3.7.1 was cleaned by a stream of hydrogen for 4 hr. at 623 K, then evacuated for 6 hr at 623 K. The catalyst was allowed to cool under vacuo to ambient temperature before building the ^{14}C - CO adsorption isotherm using ^{14}C - CO with specific activity of 0.1 mCi/mM.

The catalyst was evacuated for one hr. to determine the amount of ^{14}C - CO which can be removed by evacuation, then 12.5 torr C_2H_2 was added to the reaction vessel and the amount of ^{14}C - CO replaced from the surface by acetylene was determined. It was found (table 35) that one hr. evacuation remove 3.4% of ^{14}C - CO adsorbed species, while 12.5 torr acetylene replace 29.3% of the adsorbed ^{14}C - CO.

^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms were build up on the same catalyst sample after cleaning it by a stream of hydrogen for 4 hr at 623 K. The specific activity of ^{14}C - ethylene and ^{14}C - acetylene was the same as that of ^{14}C - CO, Fig. 10 shows a comparison between ^{14}C - CO, ^{14}C - ethylene and ^{14}C - acetylene adsorption isotherms.

3.7.1.2 ^{14}C - CO adsorption isotherm on acetylene precovered surface (Rh/SiO_2)

The same catalyst which was used in section 3.7.1 was cleaned by a stream of hydrogen for 4 hr at 623 K. The catalyst was then evacuated at 623 K for 6 hr and allowed to cool down under vacuo to ambient temperature. 12.5 torr acetylene was then admitted to this catalyst. Without removing acetylene from the gas phase the

Table 35

Effect of evacuation and acetylene on ^{14}CO adsorption isotherm

Catalyst	^{14}CO isotherm turning point (counts/min)	^{14}CO removed by evacuation (counts/min)	^{14}CO removed by acetylene (counts/min)
0.2 g Rh/SiO_2	10900	370	3194
	11100	399	3197
0.1 g Pd/SiO_2	4050	861	1501
	4000	789	1532
0.51 g Ir/SiO_2	17100	373	1155
	17200	361	1187

^{14}C - CO adsorption isotherm was build on the acetylene precovered surface. Fig. 48 shows that ^{14}C - CO adsorption on acetylene precovered surface can take place although the amount adsorbed was considerably reduced (table 42). Evacuating the reaction vessel for one hr. remove very little ^{14}C - CO (about 24 counts/min.). Addition of a pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen to the evacuated reaction vessel shows that the catalyst lost all its catalytic activity.

3.7.1.3 ^{14}C - CO adsorption isotherm on Rh/SiO_2 catalyst in the steady state.

The catalyst which was used in section 3.7.1 was cleaned by a stream of hydrogen for 4 hr at 623 K, then it was brought to the steady state by self poisoning. The catalyst in the steady state was evacuated for one hr. After which ^{14}C - CO adsorption isotherm was build. Evacuation remove very little (about 28 counts/min.) from ^{14}C - CO adsorbed species. Addition of a pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen to the evacuated reaction vessel shows that the catalyst lost all its catalytic activity. The poisoned catalyst was cleaned again, and then brought to the steady state by self poisoning. The catalyst in the steady state was evacuated for one hr, then 12.5 torr acetylene was added to the evacuated reaction vessel. Without removing the acetylene from the gas phase the ^{14}C - CO adsorption isotherm was allowed to build up by admitting small batched of ^{14}CO.

Figure 48 shows that on a catalyst in the steady state ^{14}C - CO adsorption is still taking place and leading to the formation of an

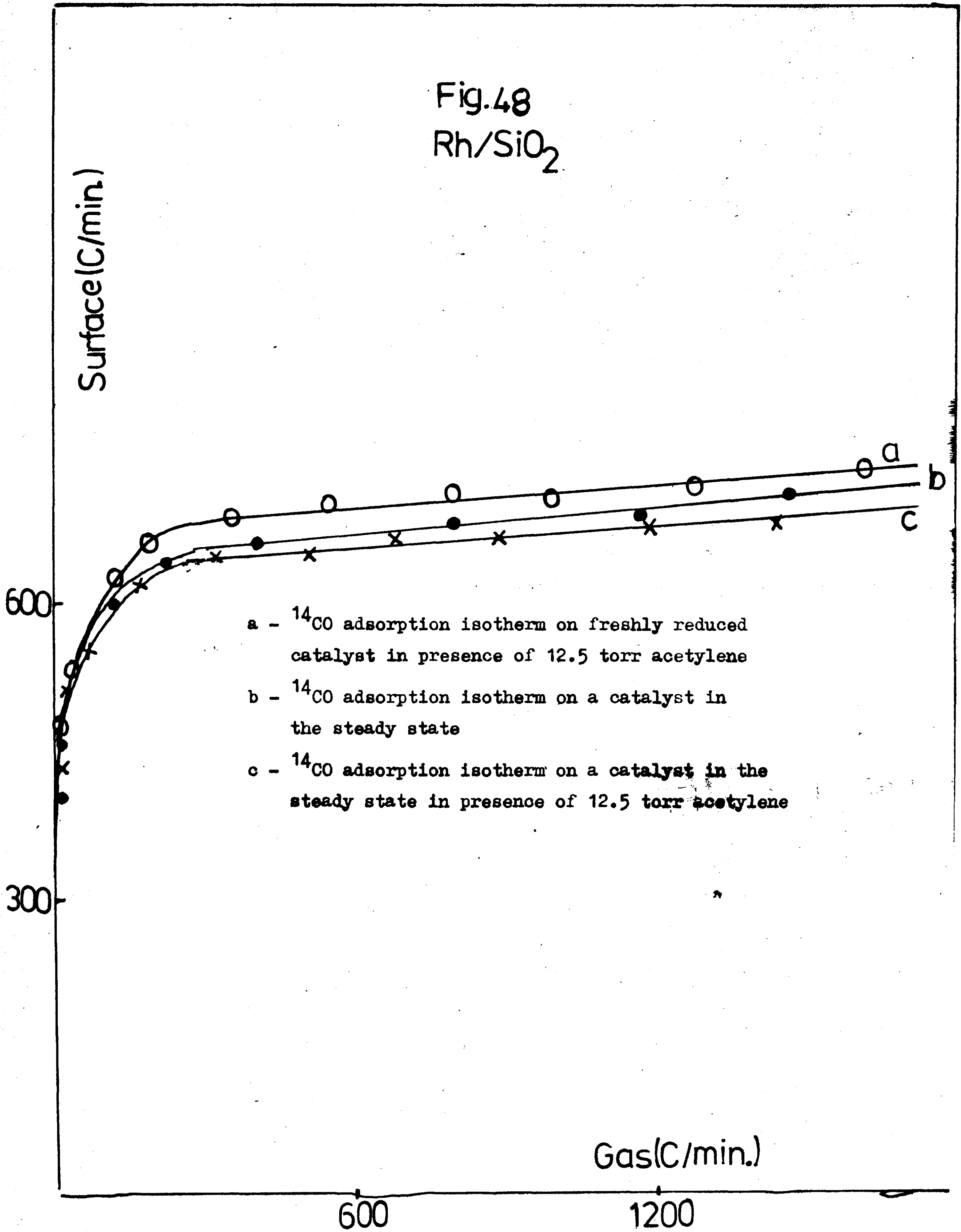


Fig.48

Rh/SiO_2

adsorption isotherm, similar in shape to that obtained using clean freshly reduced catalyst, except that the amount of ^{14}C - CO adsorbed was considerably less (table 42).

Figure 48 also shows that ^{14}C - CO adsorption, on a catalyst in the steady state, is independent of the presence or the absence of 12.5 torr acetylene in the gas phase.

3.7.1.4 ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms on CO precovered surface (Rh/SiO_2).

The catalyst which was used in section 3.7.1 was cleaned by a stream of hydrogen for 4 hr at 623 K. The catalyst was then evacuated for 6 hr. at 623 K, and allowed to cool under vacuo to ambient temperature. 5 torr non-radioactive CO was added to the reaction vessel, then without removing CO from the gas phase ^{14}C - acetylene adsorption isotherm was build. Figure 10 shows that the presence of 5 torr CO in the gas phase reduce considerably the primary region of ^{14}C - acetylene adsorption isotherm, but without having any effect on the secondary adsorption isotherm. Figure 10 shows that the presence of 5 torr CO in the gas phase prevents the formation of ^{14}C - ethylene primary region, but without having any effect on the secondary region.

3.7.2 Poisoning the acetylene hydrogenation by CO using Pd/SiO_2 catalyst.

0.1 gm Pd/SiO_2 was reduced and allowed to cool down to ambient temperature under hydrogen before a pre - mixed sample of one torr CO, 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel. It was found that the catalyst still had some catalytic activity, but this activity is very low compared to the catalytic activity of the freshly reduced catalyst.

Cleaning the catalyst by a stream of hydrogen for 4 hr at 623 K restore the catalytic activity of a freshly reduced catalyst. The prereduced catalyst was brought to the steady state by self poisoning. The effect of the presence of different quantities of CO in the gas phase on the rate of acetylene hydrogenation reaction was investigated using a catalyst in the steady state. In this investigation 12.5 torr acetylene was fist introduced to the reaction vessel, followed by a definite quanity of ^{14}CO, then 37.5 torr hydrogen was finally introduced to the reaction vessel. The reaction was followed by measuring the fall in total pressure with time.

The pressure of ^{14}CO in the gas phase inside the reaction vessel was measured during the reaction by using one of the Gieger counters inside the reaction vessel. *

The selectivity was also measured.

This experiment was repeated several times with varying pressures of CO. The results are tabulated in table 36.

Figure 49 shows the relation between the catalytic activity and the pressure of CO inside the reaction vessel.

Figure 50 shows that the hydrogenation reaction in the presence of CO is also first order with respect to the total pressure.

The results in table 36 show that the presence of CO has no effect on the selectivity of the hydrogenation reaction.

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* every 500 counts/min correspond to 0.0749 torr.

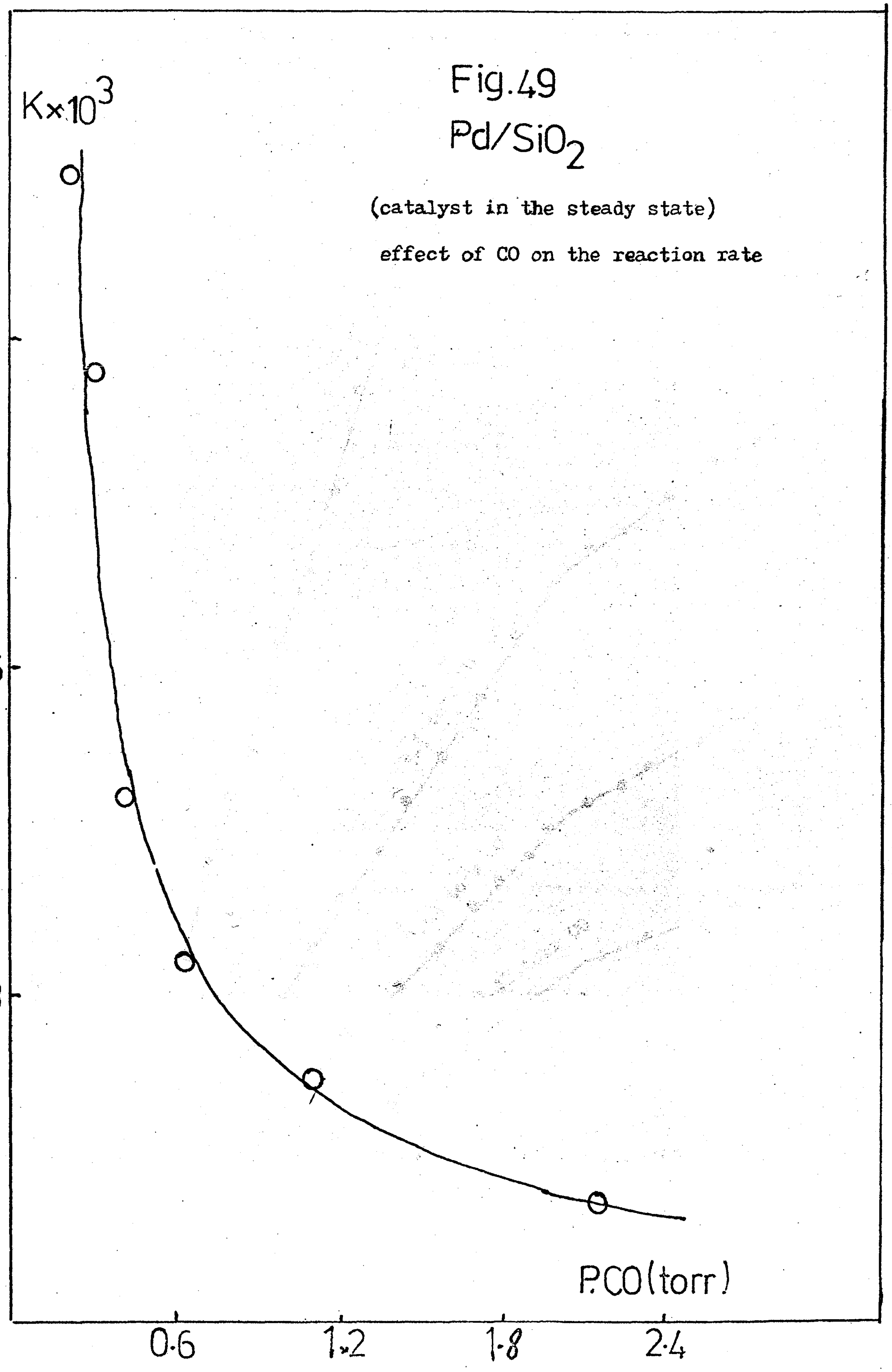


Fig.49

Pd/SiO_2

(catalyst in the steady state)

effect of CO on the reaction rate

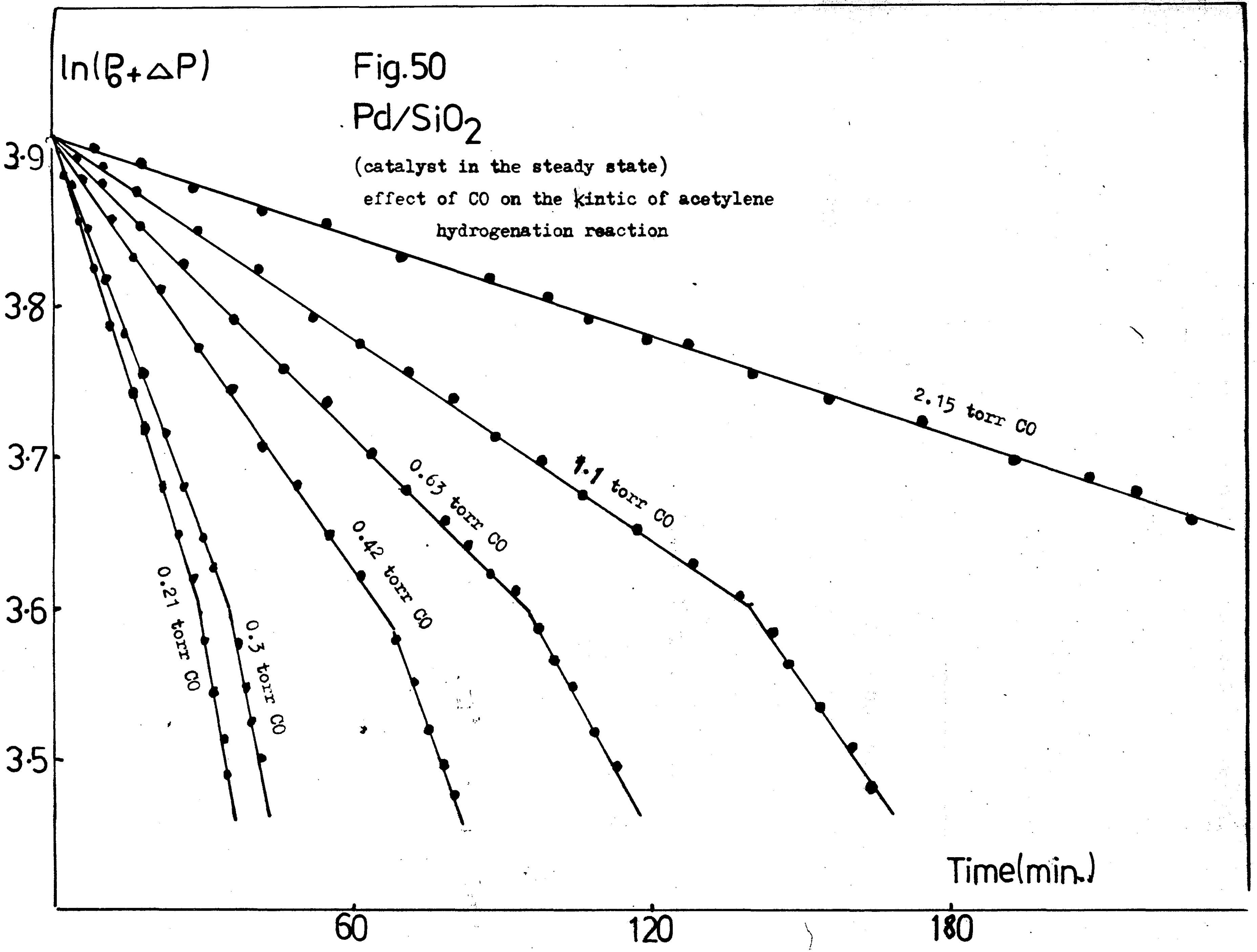


Fig.50

Pd/SiO_2

(catalyst in the steady state)

effect of CO on the kintic of acetylene hydrogenation reaction

Table 36

Effect of carbon monoxide on the reaction rate 0.1 g. Pd/SiO_2 (steady state)

Pressure of CO in the reaction vessel (torr)	Rate of reaction k min^{-1}
0	0.07308
0.212	0.01053
0.295	0.0087
0.423	0.00478
0.63	0.00328
1.1	0.00223
2.15	0.00110

3.7.2.1 ^{14}CO adsorption isotherm on a freshly reduced, clean Pd/SiO_2 surface.

The catalyst which was used in section 3.7.2 was cleaned by a stream of hydrogen for 4 hr. at 623 K. The catalyst was allowed to cool down, under vacuo, to ambient temperature before building ^{14}CO adsorption isotherm using ^{14}CO with specific activity of 0.1 mCi/mM.

The catalyst was evacuated for one hr. to determine the quantity of ^{14}CO which can be removed by evacuation. 12.5 torr acetylene was then added to the reaction vessel and the amount of ^{14}CO replaced from the surface by acetylene was measured. The results which are tabulated in table 35 show that a considerable amount of ^{14}CO was removed by evacuation and the added acetylene can remove a considerable amount of ^{14}CO from the surface.

^{14}C - ethylene and ^{14}C - acetylene adsorption isotherms were build on the same catalyst after cleaning it by a stream of hydrogen at 623 K for 4 hr. The specific activity of ^{14}C - ethylene and ^{14}C - acetylene was the same as that of ^{14}CO.

Figure 15 shows a comparison between ^{14}CO, $^{14}C_2H_2$ and $^{14}C_2H_4$ adsorption isotherms on the same catalyst sample.

3.7.2.2 ^{14}CO adsorption isotherm on acetylene precovered surface (Pd/SiO_2).

The catalyst which was used in section 3.7.2 was cleaned by hydrogen at 623 K for 4 hr and then evacuated for 6 hr at 623 K. The catalyst was allowed to cool down to ambient temperature in vacuo. 12.5 torr acetylene was added to the clean catalyst.

Without removing the acetylene from the gas phase, ^{14}CO adsorption isotherms was build.

Figure 51 shows that ^{14}CO adsorption on acetylene precovered surface was still taking place although the amount adsorbed was considerably reduced (table 42). One hr. evacuation remove all ^{14}CO which adsorbed on acetylene precovered surface.

3.7.2.3 ^{14}CO adsorption isotherm on Pd/SiO_2 catalyst in the steady state.

The catalyst which was used in section 3.7.1 was cleaned and then brought to the steady state by self poisoning. The catalyst in the steady state was evacuated for one hr. After which ^{14}CO adsorption isotherm was build.

The catalyst was cleaned again and then brought to the steady state by self poisoning.

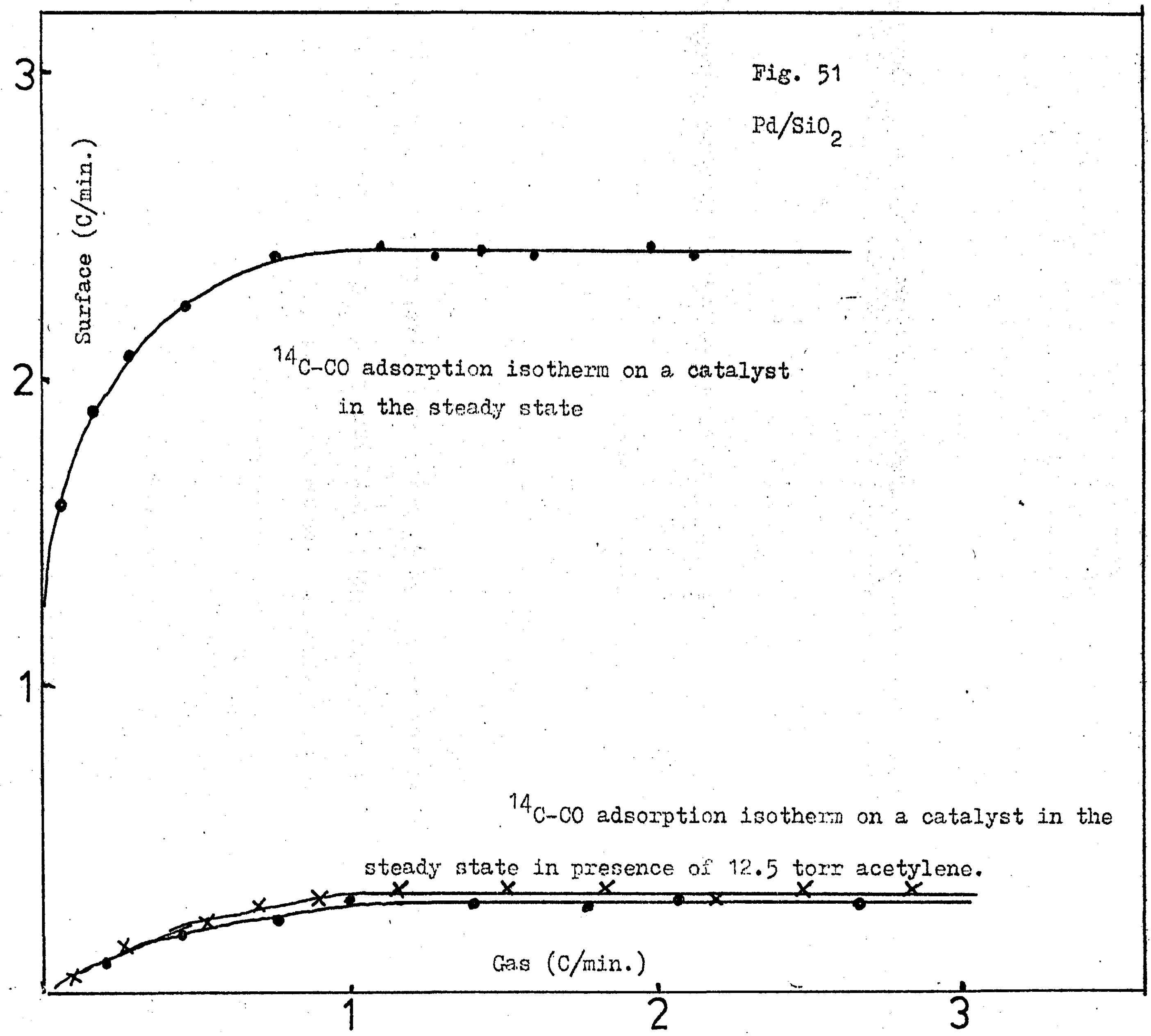
The catalyst in the steady state was evacuated for one hr, then 12.5 torr acetylene was added to the evacuated reaction vessel. Without removing the acetylene from the gas phase ^{14}CO adsorption isotherm was build.

Figure 51 shows that on a catalyst in the steady state ^{14}CO adsorption is still taking place and leading to the formation of the adsorption isotherm, similar in shape to that obtained using clean, freshly reduced catalysts, excepts that the amount of ^{14}CO adsorbed was considerably less (table 42).

Fig. 51 also shows ^{14}CO adsorption, on a catalyst in the steady state in the presence of 12.5 torr acetylene in the gas phase.

Fig. 51

Pd/SiO$_2$



3.7.2.4 ^{14}C - ethylene and ^{14}C - acetylene adsorption isotherms on CO precovered surface (Pd/SiO_2).

The catalyst which used in section 3.7.2 was cleaned by a stream of hydrogen for 4 hr at 623 K. The catalyst was then evacuated for 6 hr at 623 K, and was allowed to cool under vacuo to ambient temperature. 5 torr non-radioactive CO was added to the reaction vessel, then without removing CO from the gas phase the ^{14}C - acetylene adsorption isotherm was build.

Figure 15 shows that the presence of 5 torr CO in the gas phase reduce considerably the primary region of ^{14}C - acetylene adsorption isotherm, but without having any effect on the secondary adsorption region.

Figure 15 also shows that the presence of 5 torr CO in the gas phase prevent the formation of ^{14}C - ethylene primary region, but without having any effect on the secondary region.

3.7.3 Poisoning the acetylene hydrogenation by CO using Ir/SiO_2 catalyst.

0.51 gm Ir/SiO_2 was reduced and allowed to cool down to ambient temperature before evacuation. A pre - mixed sample of one torr CO, 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel. It was found that no reaction took place although the reaction mixture was kept over the catalyst for 12 hr. the reaction mixture was removed by one hr. evacuation, then a pre - mixed sample containing only 12.5 torr acetylene and 37.5 torr hydrogen was introduced to the reaction vessel; no reaction was observed to take place. The poisoned catalyst was cleaned by a stream of hydrogen for 4 hr at 623 K, then was allowed to cool down to ambient temperature before evacuation. To this prereduced catalyst a pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen was added. The catalyst shows very high catalytic activity which is the same as that of a freshly reduced catalyst. The prereduced catalyst was brought to the steady state by self poisoning. To this deactivated catalyst a pre - mixed sample of one torr CO, 12.5 torr acetylene and 37.5 torr hydrogen was added; no reaction was observed to take place.

The catalytic activity of this poisoned catalyst cannot be restored by evacuating the reaction vessel for one hr, but it can be restored by cleaning the catalyst by a stream of hydrogen for 4 hr at 623 K.

3.7.3.1 ^{14}CO adsorption isotherm on a freshly reduced, clean Ir/SiO_2 surface.

The catalyst which was used in section 3.7.3 was cleaned by a stream of hydrogen for 4 hr at 623 K, then evacuated for 6 hr at 623 K. The catalyst was allowed to cool down under vacuo to ambient temperature before building ^{14}CO adsorption isotherm using ^{14}CO with specific activity of 0.1 mCi/mM. The catalyst was evacuated for one hr. to determine the amount of ^{14}CO which can be removed by evacuation, then 12.5 torr acetylene was added to the reaction vessel and the amount of ^{14}CO replaced from the surface by acetylene was determined. It was found (table 35) that one hr. evacuation removed about 2% of ^{14}CO adsorbed species, while 12.5 torr acetylene replaced 6.8% of the adsorbed ^{14}CO.

Figure 18 shows a comparison between ^{14}CO, ^{14}C - ethylene and ^{14}C - acetylene adsorption isotherms on the same catalyst sample.

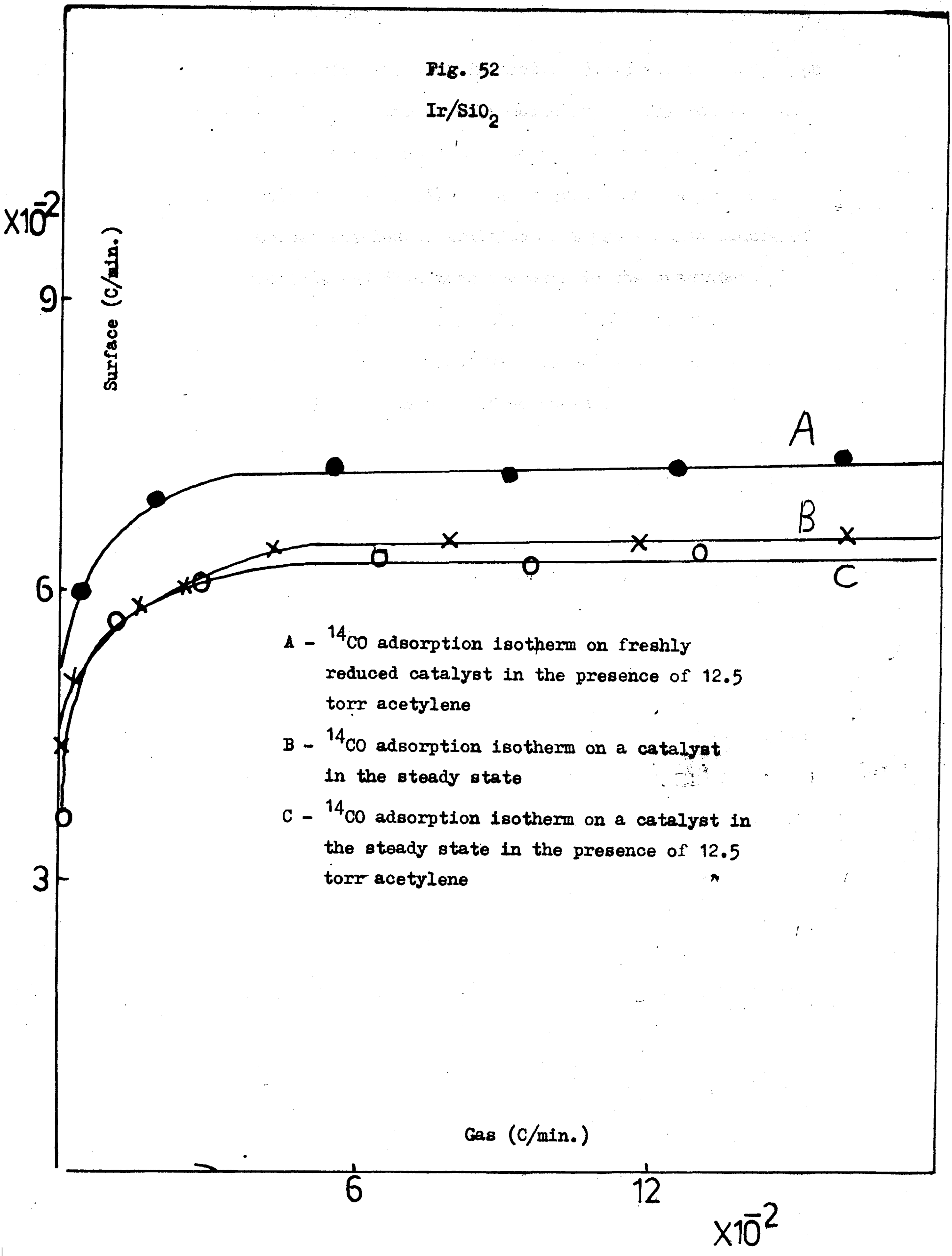
3.7.3.2 ^{14}CO adsorption isotherm on acetylene precovered surface (Ir/SiO_2).

The same catalyst which was used in section 3.7.3 was cleaned by a stream of hydrogen for 4 hr at 623 K. The catalyst was then evacuated at 623 K for 6 hr and allowed to cool down to ambient temperature. 12.5 torr acetylene was then admitted to this catalyst. Without removing acetylene from the gas phase ^{14}CO adsorption isotherm was build on the acetylene precovered surface.

Figure 52 shows that ^{14}CO adsorption on the acetylene precovered surface can take place although the amount adsorbed was considerably reduced (table 42). Evacuating the reaction vessel removed none of ^{14}CO which was adsorbed on acetylene precovered surface.

Fig. 52

Ir/SiO_2



A - ^{14}CO adsorption isotherm on freshly reduced catalyst in the presence of 12.5 torr acetylene

B - ^{14}CO adsorption isotherm on a catalyst in the steady state

C - ^{14}CO adsorption isotherm on a catalyst in the steady state in the presence of 12.5 torr acetylene

3.7.3.3 ^{14}CO adsorption isotherm on Ir/SiO_2 catalyst in the steady state.

The catalyst which was used in section 3.7.3 was cleaned, then brought to the steady state by self poisoning. The catalyst in the steady state was evacuated for one hr, after which ^{14}CO adsorption isotherm was build. One hr evacuation remove none from ^{14}CO adsorbed species. Addition of a pre - mixed sample of 12.5 torr acetylene and 37.5 torr hydrogen to the evacuated reaction vessel shows that the catalyst lost all its catalytic activity. The poisoned catalyst was cleaned again, and then brought to the steady state by self poisoning.

The catalyst in the steady state was evacuated for one hr, then 12.5 torr acetylene was added to the evacuated reaction vessel. Without removing the acetylene from the gas phase ^{14}CO adsorption isotherm was build.

Figure 52 shows that, on a catalyst in the steady state, ^{14}CO adsorption is still taking place and leading to the formation of an adsorption isotherm, similar in shape to that obtained using a clean freshly reduced catalyst, except that the amount of ^{14}CO adsorbed was considerably less (table 42).

Fig. 52 also show that ^{14}CO adsorption, on a catalyst in the steady state, is independent of the presence or the absence of 12.5 torr acetylene in the gas phase.

3.7.3.4 ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherm on CO precovered surface (Ir/SiO_2).

The catalyst which was used in section 3.7.3 was cleaned by a stream of hydrogen for 4 hr at 623 K. The catalyst was then evacuated for 6 hr at 623 K, and was allowed to cool under vacuo to ambient temperature. 5 torr non-radioactive CO was added to the reaction vessel, then without removing CO from the gas phase ^{14}C - acetylene adsorption isotherm was build. Figure 18 shows that the presence of 5 torr CO in the gas phase reduce considerably the primary region of ^{14}C - acetylene adsorption isotherm, but without having any effect on the secondary adsorption isotherm.

Figure 18 also shows that the presence of 5 torr CO in the gas phase prevents the formation of ^{14}C - ethylene primary region, but without having any effect on the secondary region.

3.8 The Support Effect.

3.8.1 The catalytic properties of Pd/Al_2O_3.

From the results described in the previous section it is apparent that there are some general similarities between the catalytic properties of Rh, Ir and Pd supported on SiO_2. These similarities can be seen from the shapes of ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms and the effects of deactivation and other experimental variables on these isotherms. In order to examine the possibility that these general similarities are inherent properties of the metal rather than of the SiO_2 support; it was decided to use Al_2O_3 as a support to study the catalytic behaviour of Pd/Al_2O_3. It was hoped that by comparing the catalytic behaviour of Pd/Al_2O_3 with that of Pd/SiO_2 the effects of the support could be isolated and therefore, the common catalytic properties shown by different metal catalysts could be established.

5% Pd/Al_2O_3 was prepared in exactly the same way as that used for preparing 5% Pd/SiO_2.

0.005 g Pd/Al_2O_3 was used to study the overall kinetics of the reaction, the deactivation by self - poisoning, the selectivity and the effects of added ^{14}C - ethylene on the selectivity. All these experiments were performed using exactly the same procedure as that used with Pd/SiO_2 catalyst.

Figure 53 shows some typical pressure fall against time curves which are exactly the same as those observed with Pd/SiO_2.

Up to the acceleration point the pressure - time curves were always accurately first order in total pressure (figure 54).

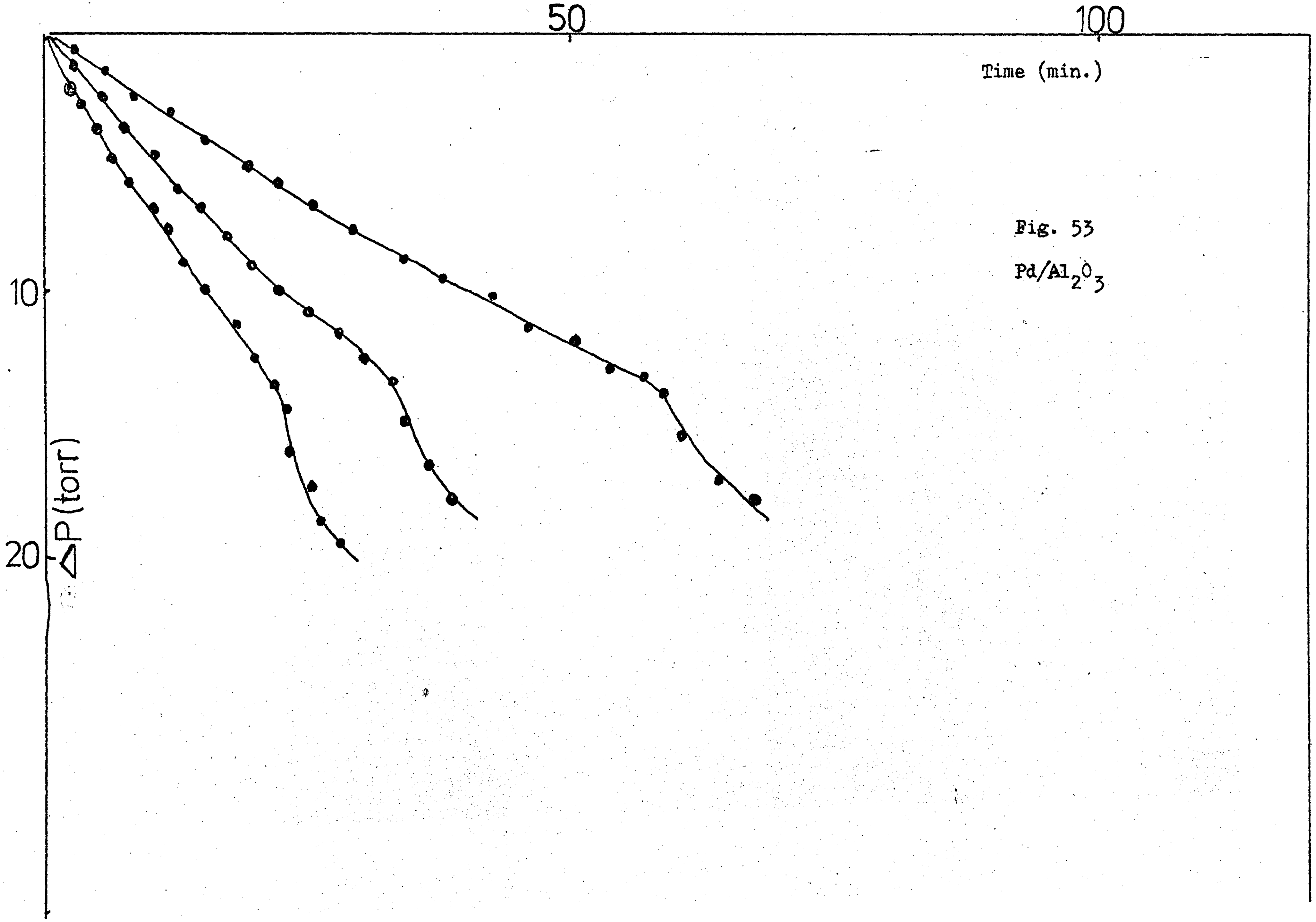
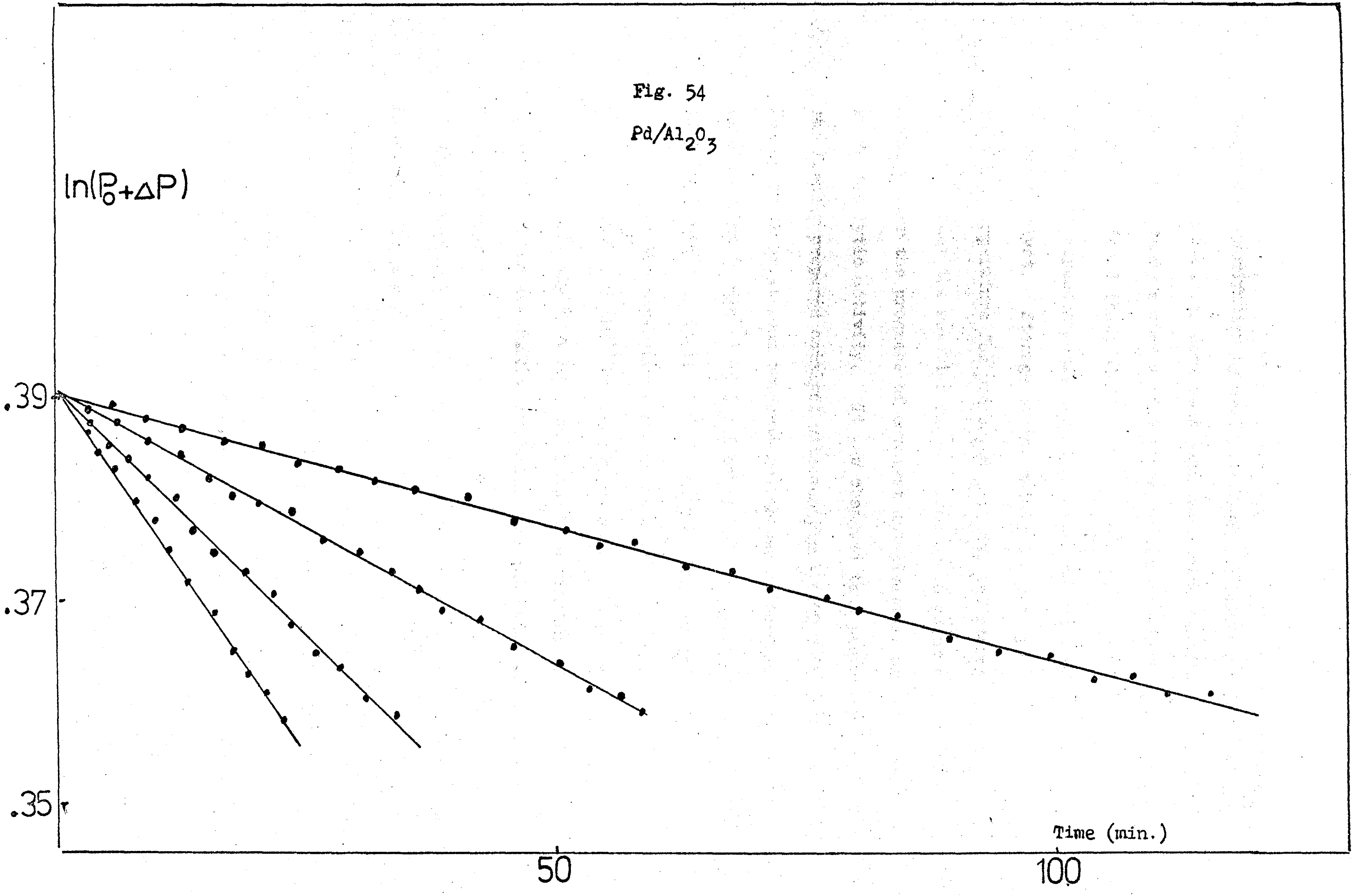


Fig. 53

Pd/Al_2O_3

Fig. 54

Pd/Al_2O_3



Just as in the case of Pd/SiO_2, the freshly reduced Pd/Al_2O_3 underwent deactivation by self poisoning. Figure 6 shows that the rate of the reaction decreased with successive reactions until a constant "steady state" activity was eventually attained.

It was found that, similar to Pd/SiO_2, the deactivation process was dependent only upon the number of reactions performed on the catalyst. Storage of the catalyst under hydrogen at the reaction temperature for prolonged periods, and storage of the catalyst under the reaction products for up to 48 hr had no effect upon, either the progress of catalyst deactivation, or the steady state catalytic activity. It was observed that pretreatment of the freshly prepared catalyst with acetylene (100 torr acetylene for up to 12 hr at room temperature) showed a decrease in the rate constant (k min^{-1}) of the freshly reduced catalyst from 14.5×10^{-3} min^{-1} to 13.1×10^{-3} which is small compared to the decreased in the catalytic activity caused by self poisoning (k min^{-1} of 1.5×10^{-3} min^{-1} at the steady state). The selectivity was decreased only by a very small amount during the process of deactivation and eventually reached a constant value at the steady state (table 37).

The selectivity at the steady state for both Pd/SiO_2 and Pd/Al_2O_3 is exactly the same.

The catalytic activity of the freshly prepared catalyst could be reproducibly restored by heating the catalyst in an atmosphere of hydrogen for one hr at 623 K.

Table 4 shows that the regeneration process is reproducible and independent of the period of heating the catalyst at 623 K under hydrogen for periods in excess of 1 hr.

The selectivity of acetylene hydrogenation reaction was

Table 37

0.005 g : Pd/Al_2O_3

Effect of self - poisoning on selectivity

reaction number	selectivity
2	0.9545
5	0.9537
7	0.9521
11	0.9481
13	0.9431
15	0.9416
16	0.9409
17	0.9401
18	0.9404

Table 38

0.005 g Pd/Al_2O_3

% conversion	PC_2H_4 (torr)	PC_2H_6 (torr)	selectivity
20.7	2.01	0.127	0.9402
31.2	2.90	0.186	0.9400
41.6	3.70	0.233	0.9408
56.1	4.93	0.313	0.9401
73.5	6.51	0.417	0.9401
89.7	7.87	0.510	0.9390

measured at various conversions using a catalyst in the steady state (table 38).

The effect of added ^{14}C - ethylene upon the acetylene hydrogenation reaction was examined by addition of a pre - mixed sample of about 10 torr ^{14}C - ethylene, 12.5 torr acetylene and 37.5 torr hydrogen to the catalyst. The results (table 39) show that as in the case of Pd/SiO_2 the ^{14}C - ethylene can be hydrogenated in the presence of acetylene to ^{14}C - ethane. This hydrogenation takes place very slowly compared to the fast hydrogenation of ethylene in the absence of acetylene.

Figure 55 shows that the plot of the quantity of ^{14}C - ethane against % conversion yield a straight line. This indicates that the hydrogenation of ^{14}C - ethylene proceeded independently of the quantity of acetylene in the reaction vessel.

0.1 g Pd/Al_2O_3 was used to study the effect of deactivation and other experimental variables on the ^{14}C - ethylene and ^{14}C - acetylene adsorption isotherms.

Figure 56 shows that the ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms on a clean, freshly reduced surface consist of a non - linear primary region followed by a linear secondary region.

It was found that 24% of ^{14}C - acetylene primary region was retained after treating the catalyst with 50 torr (1:3) C_2H_2; H_2 mixture.

Similar treatment to ^{14}C - ethylene primary region left 62% of the adsorbed species retained on the surface.

In the case of freshly reduced Pd/Al_2O_3 the analysis of the gas phase in equilibrium with the surface at various stages during the adsorption of ^{14}C - acetylene showed that ethane was

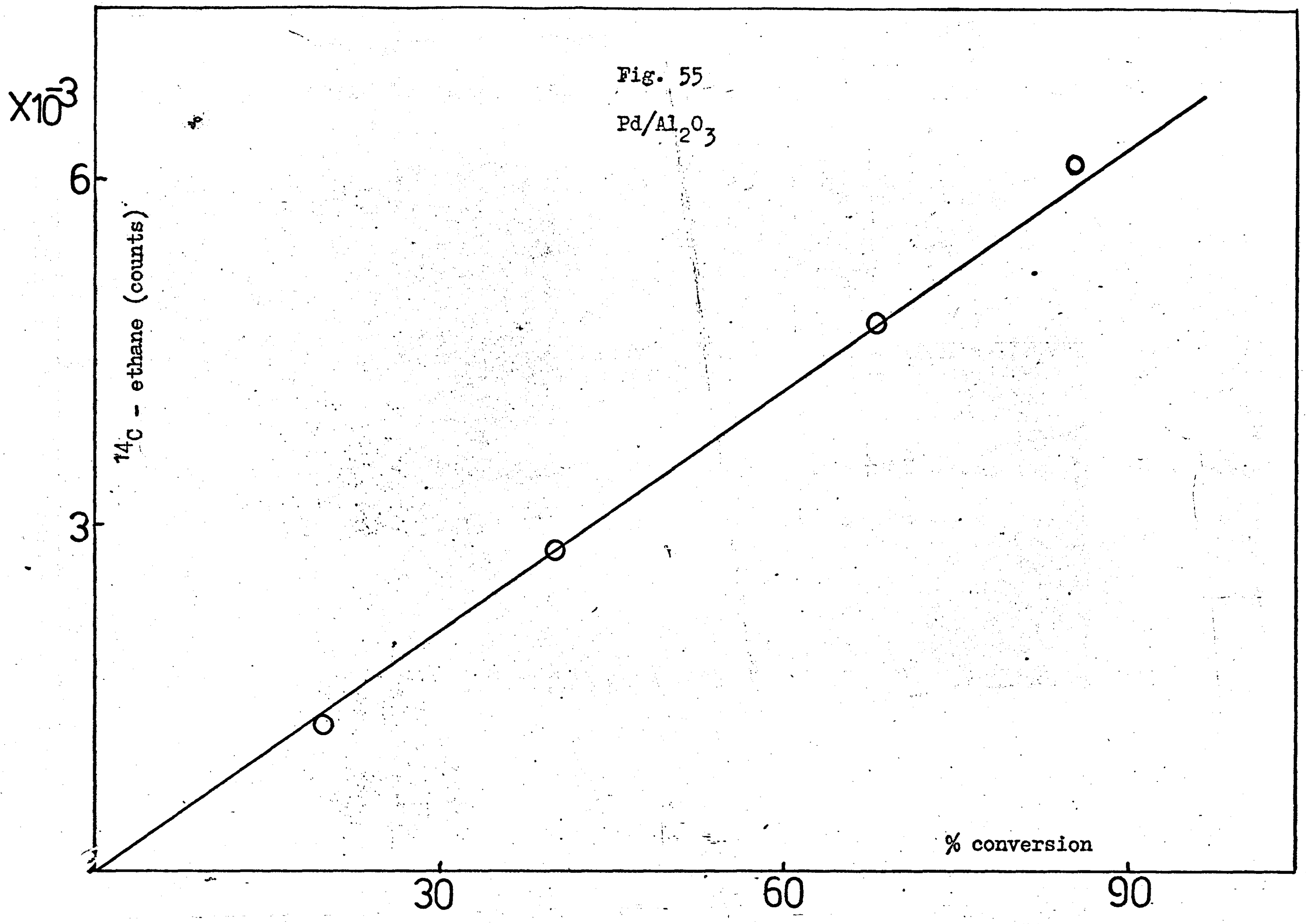


Fig. 55

Pd/Al_2O_3

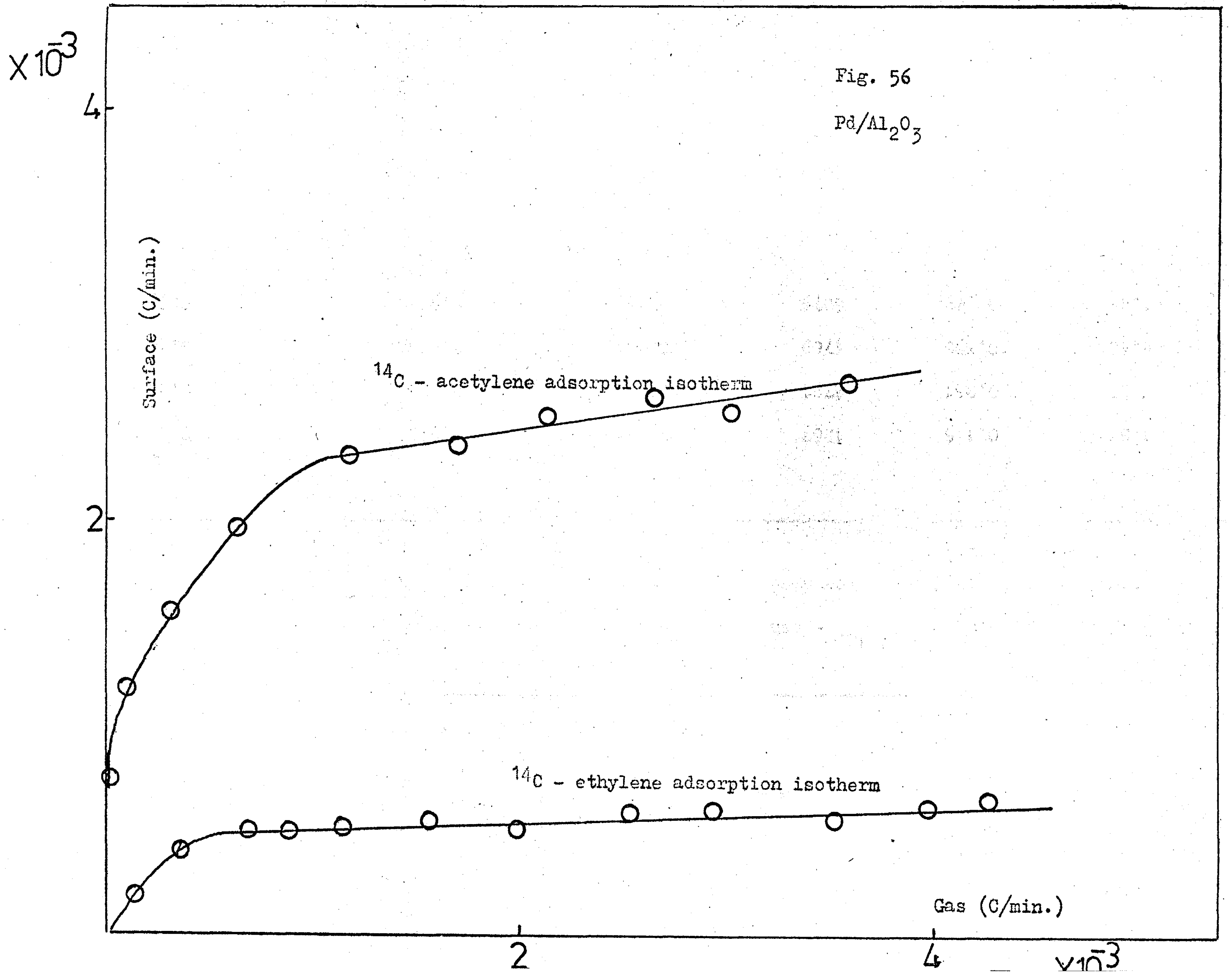


Fig. 56

Pd/Al_2O_3

Table 39

10.2 torr ^{14}C - ethylene (0.005gm Pd/Al_2O_3)

% conversion	PC_2H_4 (torr)	PC_2H_6 (total) (torr)	^{14}C - ethane (counts)	$P^{14}C_2H_6$ (torr)	$S = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6}$	$S' = \frac{PC_2H_4}{PC_2H_4 + PC_2H_6 - P^{14}C_2H_6}$
Exp. 1						
20.1	1.82	0.115	1267	0.0279	0.9272	0.9406
39.8	3.61	0.231	2791	0.0614	0.9253	0.9401
68.5	6.14	0.390	4769	0.1049	0.9254	0.9403
85.6	7.41	0.479	6079	0.1338	0.9235	0.9392
Exp. 2						
22.7	2.01	0.128	1439	0.0317	0.9264	0.9402
42.3	3.89	0.243	3002	0.066	0.9264	0.9413
56.8	5.09	0.325	3768	0.0829	0.9258	0.9400
74.9	6.68	0.430	5213	0.1147	0.9246	0.9395

the only gaseous species present up to a point corresponding to 74.9% of the total primary adsorption region. During the subsequent build up of the isotherm the gas consisted of the ethane, formed in the primary region, and acetylene. No ethylene was observed to be formed at any stage during the adsorption of acetylene (fig. 57). Similar analysis during the ^{14}C - ethylene adsorption showed that only ethane was present in the gas phase during the build up of the primary region; ethylene only appeared in the gas phase at the commencement of the secondary region.

The formation of ethane ceased at the onset of the secondary region (figure 58).

With Pd/Al_2O_3 in the steady state the analysis of the gas phase in equilibrium with the surface showed that during the build up of ^{14}C - acetylene and ^{14}C - ethylene adsorption isotherms, no ^{14}C - ethane was present in the gas phase.

It was observed also that the catalyst which had been activated by hydrogen at 623 K, but which had been allowed to cool down to ambient temperature in hydrogen before evacuation, rather than evacuated at 623 K, showed similar adsorption isotherms, except that the extent of the primary adsorption was substantially reduced (table 6) and that all the adsorbed species on the primary region can be removed by 37.5 torr hydrogen mixed with 12.5 torr acetylene.

The catalytic activity and the secondary region were not affected by changing the temperature at which the catalyst was evacuated.

Fig. (59) shows that the effect of self poisoning was to reduce considerably the extent of the ^{14}C - acetylene primary region without having any observable effect on the secondary adsorption process.

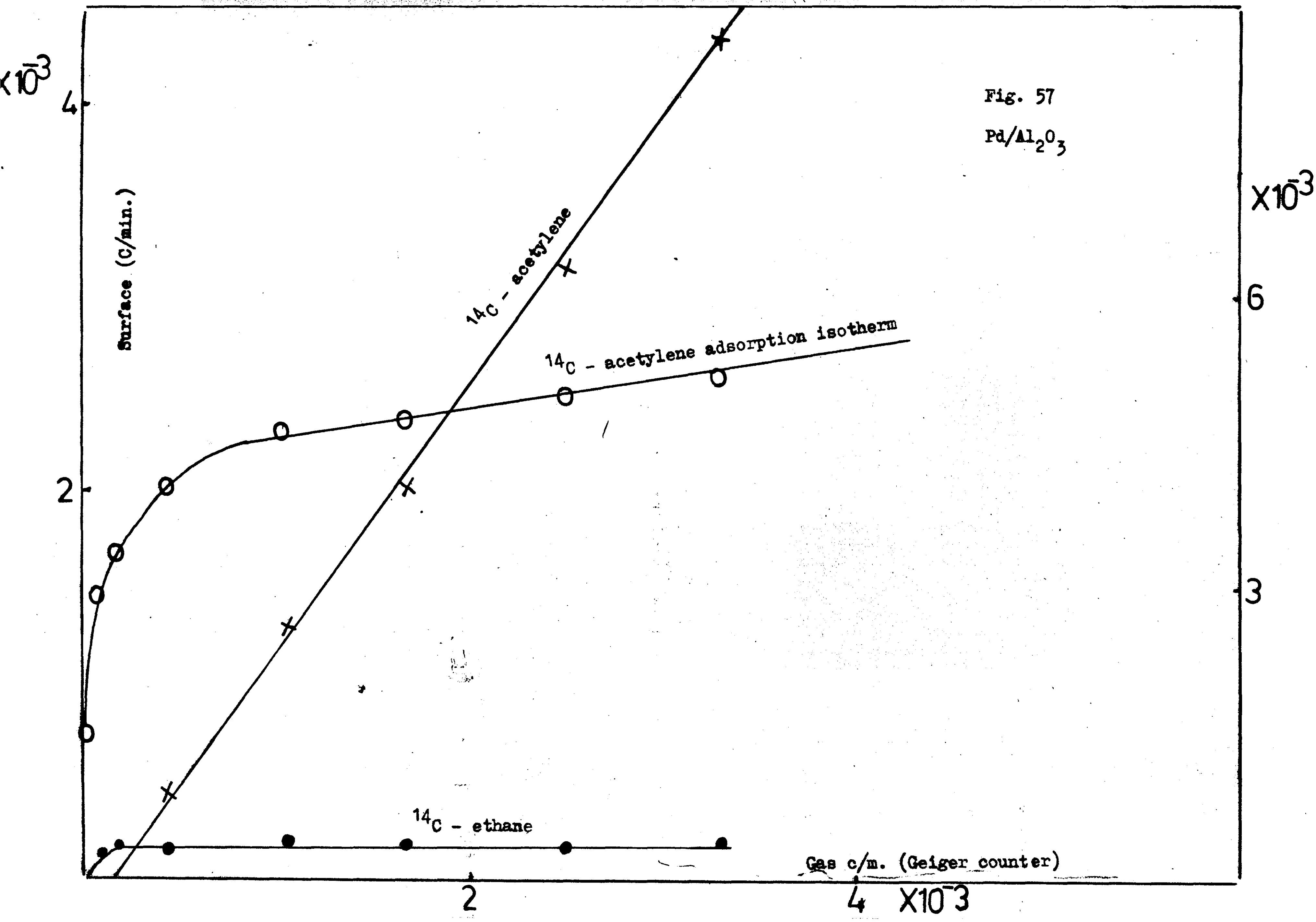


Fig. 57

Pd/Al_2O_3

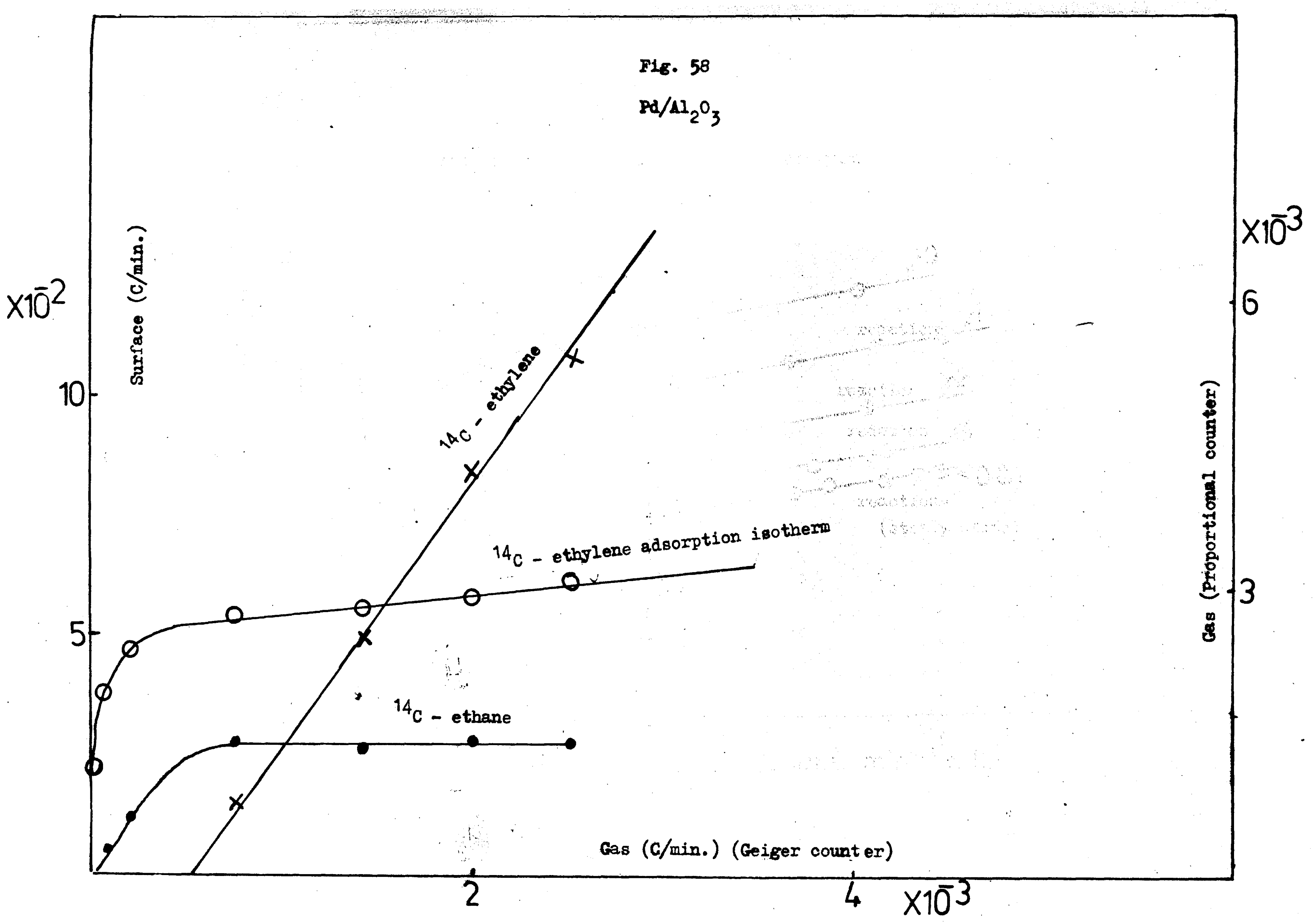


Fig. 58

Pd/Al_2O_3

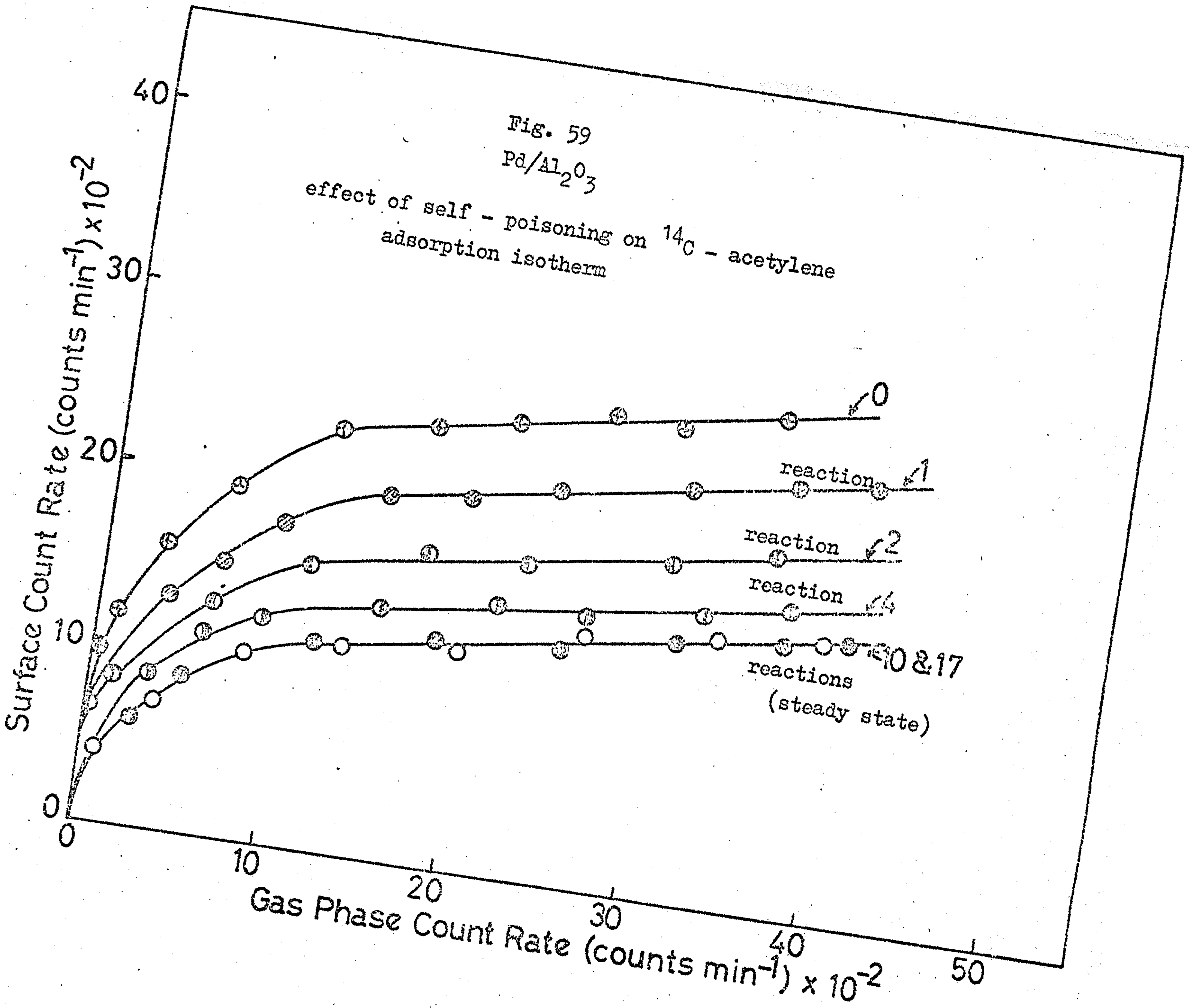


Fig. 59

Pd/Al_2O_3

effect of self - poisoning on ^{14}C - acetylene adsorption isotherm

Figure 60 shows that the effect of the deactivation of the catalyst by self poisoning was to reduce the extent of ^{14}C - ethylene primary region until it disappeared completely as the steady state activity is reached. It also shows that the deactivation has no observable effect on ^{14}C - ethylene secondary adsorption process. Some of the experimental results are shown in Table 33.

The results of all the experiments show that Pd/Al_2O_3 behaves in a similar way to Pd/SiO_2.

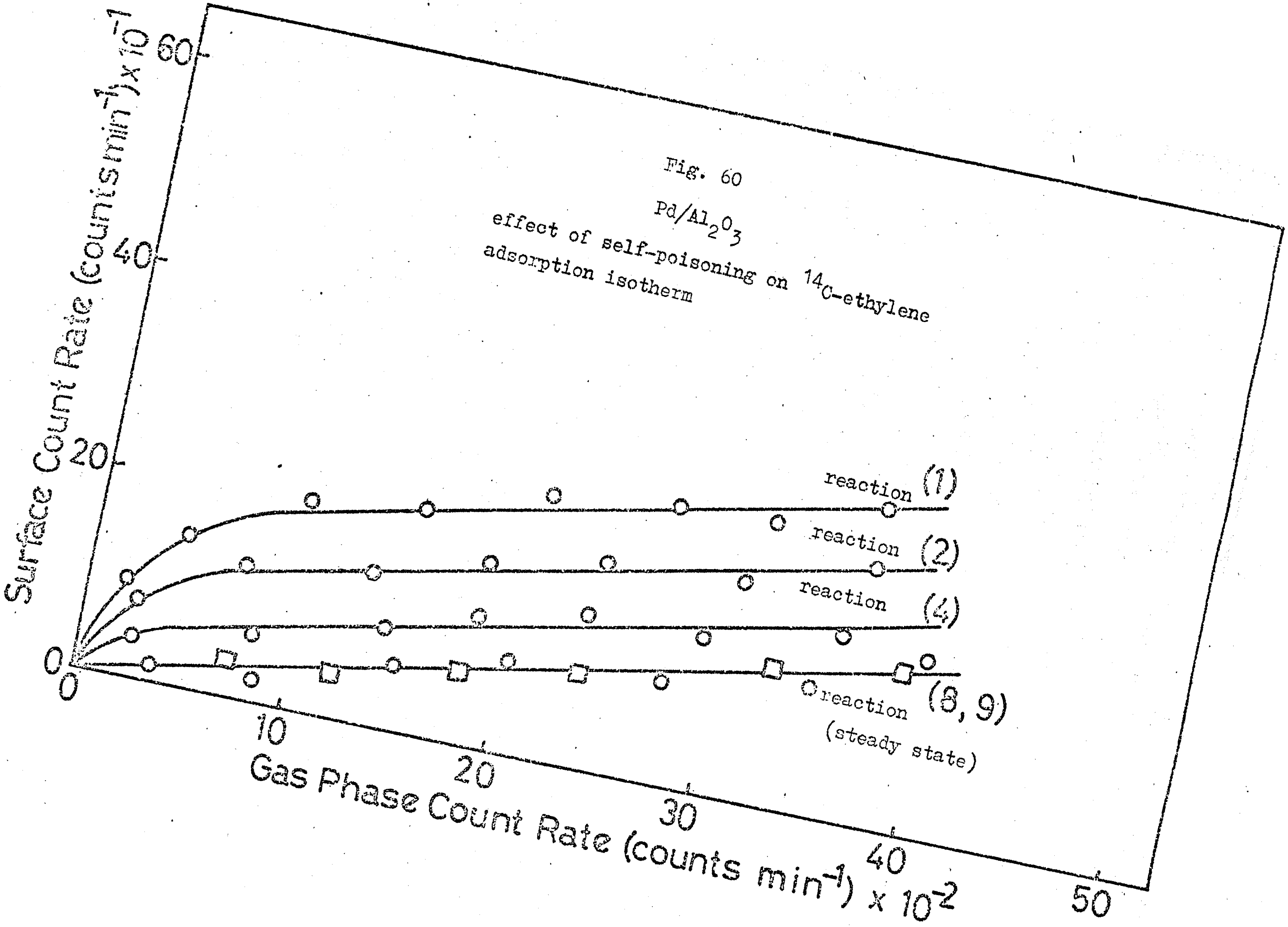


Fig. 60

Pd/Al_2O_3

effect of self-poisoning on ^{14}C-ethylene adsorption isotherm

3.8.2 ^{14}C - acetylene adsorption isotherm on 5% Rh/Silylated SiO_2.

From the experimental results in the previous sections it was observed that ^{14}CO adsorption isotherms on Rh/SiO_2, Ir/SiO_2 and Pd/SiO_2 show Langmuir type behaviour, consisting of steep primary region followed by a secondary region with zero gradient, while the adsorption isotherms of ^{14}C - acetylene and ^{14}C - ethylene contain in addition to the primary region a linear secondary region with a positive gradient.

By considering that CO was only adsorbed on the metal Reid and Webb (2) proposed that the primary region of ^{14}C - ethylene and ^{14}C - acetylene occurs on the metal while the secondary region occurs on SiO_2 or Al_2O_3 supports, and that the hydroxyl groups associated with the SiO_2 and Al_2O_3 supports is the site where acetylene and ethylene can be adsorbed during the build up of the secondary region.

To test this hypothesis it was decided to use Rh catalysts supported on SiO_2 in which all the hydroxyl groups had been replaced by an inert trimethyl silyl group (- Si $(CH_3)_3$).

To replace the - OH group by - $Si(CH_3)_3$ group the experimental procedure proposed by Kung and Brooks (147) was used. According to this procedure, 25 gm SiO_2 were suspended in a mixture of 80 ml of light petroleum (bp 60 - 80°) and 15 ml of hexamethyldisilazane. The mixture was heated on a steam - bath and refluxed for 1 hr. A drying tube of calcium sulphate was used at the condenser exit. After refluxing, 2 ml of n - propanal were added. This helps materially be wetting the SiO_2, and although it reacts with unchanged hexamethyldisilazane to form $SiMe_3OP$, this in turn reacts with the hydroxyl groups in the same way as the parent silazane. After 30 hr. the mixture was again refluxed for 6 hours. The SiO_2 was then washed with light petroleum (2 × 50 ml), then n - propanal (1 × 50 ml). Finally, it was dried for 2 hr. at 100 °C in an oven. This silylated SiO_2 was used to prepare a 5% Rh/silylated SiO_2 catalyst using exactly the same procedure which used to prepare 5% Rh/SiO_2 (see section 2.2).

0.2 g of the supported salt was reduced by using the same method used with Rh/SiO_2.

Figure 61 shows that ^{14}C - acetylene adsorption isotherm on 5% Rh/silylated SiO_2 is within experimental error exactly similar to those obtained using the untreated 5% Rh/SiO_2.

$$\text{The ratio of } \frac{\text{gradient of } ^{14}\text{C - acetylene secondary region}}{\text{amount of primary adsorption region}} = \frac{1.12}{5437}$$

$$= 2.06 \times 10^{-4} \text{ (Rh/silylated SiO}_2\text{)}$$

$$\text{with Rh/SiO}_2 \quad \frac{\text{gradient of } ^{14}\text{C-acetylene secondary region}}{\text{amount of primary adsorption region}} = \frac{1.25}{5688} = 2.19 \times 10^{-4}$$

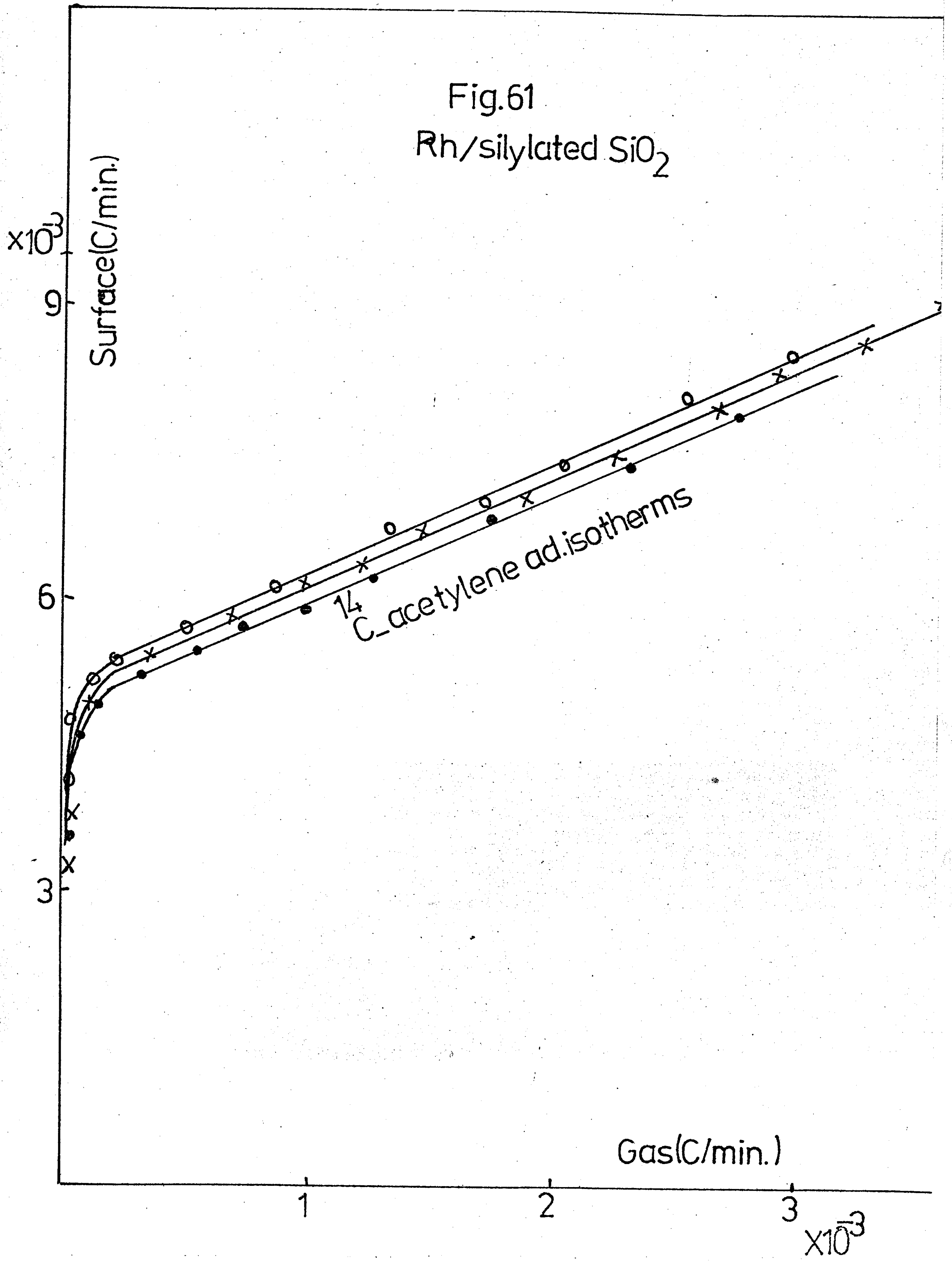


Fig.61
Rh/silylated SiO$_2$
x10^{-3}
Surface(C/min.)
9
6
3
^{14}C_acetylene ad.isotherms
Gas(C/min.)
1
2
3
X10^{-3}

CHAPTER FOUR

DISCUSSION

Introduction

From the results presented in chapter 3 a number of interesting and important features emerge regarding the adsorption of acetylene, ethylene and carbon monoxide.

The adsorption isotherms of acetylene and ethylene on freshly reduced catalysts show that the adsorptions occur in two distinct regions, a non-linear "primary" followed by a linear "secondary" region. Similar results have been reported previously (43) for acetylene and ethylene adsorption on silica - and alumina - supported rhodium catalysts.

In contrast to acetylene and ethylene adsorption, carbon monoxide adsorption showed typical Langmuir - type behaviour. With each of the catalysts it was found that the rate of acetylene hydrogenation decreased with successive reactions until a constant "steady state" activity was eventually attained. The reaction rate did not tend to zero.

It was observed that pretreatment of the freshly prepared catalysts with 100 torr acetylene for up to 12 hr at room temperature produced only a negligible decrease in the rate constant ($k\,\mathrm{min}^{-1}$) of the freshly reduced catalysts. Deactivation could only be achieved using acetylene - hydrogen reaction mixtures. Once the steady state had been achieved the storage of the catalysts under hydrogen for prolonged periods, or storage of the catalyst under the reaction products for up to 72 hr had no effect on the steady state catalytic activity.

On catalysts in their steady states the acetylene and ethylene isotherms showed a reduced (C_2H_2 on Pd) or no primary region.

Deactivation had no observable effect on the secondary region for any of the catalysts.

The presence of one torr carbon monoxide in the reaction mixture effectively poisons the acetylene hydrogenation reaction over both freshly reduced and steady state Rh/SiO_2 and Ir/SiO_2 catalysts, although with palladium/silica only a partial reduction in activity occurs.

Addition of ^{14}C - ethylene to the acetylene hydrogenation mixture causes an increase in the ethane yield which, from the yield of ^{14}C - ethane, is directly proportional to the amount of added ^{14}C - ethylene.

These observations will each be discussed in detail in the ensuing sections.

4.1 The ^{14}C - acetylene primary adsorption isotherm:

The results of sections 3.2 and 3.8.1 show that with Rh/SiO_2 and Ir/SiO_2 the analysis of the gas phase in equilibrium with the surface of the freshly reduced catalyst at various stages during the adsorption of ^{14}C - acetylene showed that ethane was the only gaseous species present during the build up of the primary region. The formation of ethane ceased at the onset of the secondary adsorption region.

In the case of Pd/SiO_2 and Pd/Al_2O_3 the analysis of the gas phase in equilibrium with the surface of the freshly reduced catalyst at various stages during the adsorption of ^{14}C - acetylene showed that ethane was the only gaseous species present up to a point corresponding to 74.9% (Pd/Al_2O_3) or 80.5% (Pd/SiO_2) of the total primary adsorption region.

During the subsequent build up of each isotherm the gas consisted of the ethane, formed in the primary region, and acetylene. Ethylene was never observed as a product resulting from the adsorption of acetylene.

Table 40 shows the number of ^{14}C - acetylene molecules adsorbed on the primary region; the total number of metal atoms in the catalyst; the number of ^{14}C - ethane molecules formed during the build up of the primary region and the total number of ^{14}C - carbon monoxide adsorbed on the primary region.

From the yields of ethane the average composition of the adsorbed acetylenic species on the primary region can be calculated to be $C_2H_{1.4}$(Pd); $C_2H_{1.8}$ (Rh) and $C_2H_{1.6}$ (Ir), assuming that, as observed previously (39, 148), the amount of catalyst hydrogen

Table 40

catalyst	number of metal atoms	number of C_2H_2 molecules	number of C_2H_6 molecules	number of CO molecules	H/C ratio
0.2g Rh/SiO_2	5.84×10^{19}	1.23×10^{19}	0.592×10^{18}	2.40×10^{19}	1.8/2
0.1g Pd/SiO_2	2.83×10^{19}	0.498×10^{19}	0.891×10^{18}	0.662×10^{19}	1.4/2
0.51g Ir/SiO_2	7.99×10^{19}	1.99×10^{19}	1.46×10^{18}	4.26×10^{19}	1.6/2

available for hydrogenation is negligible. These values were constant throughout the entire primary region.

These results suggest that the acetylene adsorbed on the primary region is predominantly a dissociatively adsorbed species, which may possibly be present as a surface polymers, as suggested from previous studies (40, 42, 120, 121, 119, 149, 150).

It has been observed in the present work that with Rh/SiO_2, Pd/SiO_2 and Ir/SiO_2 the presence of carbon monoxide on the surface of the freshly reduced catalysts reduces considerably the extent of ^{14}C - acetylene primary region (figures 10, 15 and 18). Conversely, the presence of 12.5 torr acetylene in the gas phase, before admission of the ^{14}C - carbon monoxide, was found to reduce the extent of ^{14}C - carbon monoxide on freshly reduced catalysts by more than 90% (Table 41). If, as appears to be the case from previous studies (151, 152), it is assumed that the carbon monoxide is specifically adsorbed on the metal, the above experimental observations suggest that ^{14}C - acetylene primary adsorption occurs directly on the exposed metal and the turning point in the acetylene adsorption isotherm corresponds to monolayer coverage of the metal with hydrocarbon.

Catalysts which had been activated, but which had been allowed to cool to ambient temperature in hydrogen before evacuation, rather than evacuated at 623 K for 6 hr., showed similar adsorption isotherms to those in figures 10, 15 and 18, except that the extent of the primary adsorption was substantially reduced (Table 6). This shows that the effect of preadsorbed hydrogen, assumed to be present after the catalyst was allowed to cool to ambient temperature in hydrogen before evacuation, was to reduce the extent of the primary region.

Table 41

Effect of acetylene on CO adsorption

Catalyst (freshly reduced)	turning point of ^{14}CO isotherm in the absence of acetylene (counts/min.)	turning point of ^{14}CO isotherm in the presence of 12.5 torr (counts/min.)
0.1 gm Pd/SiO_2	4050	320
0.2 gm Rh/SiO_2	11100	685
0.51 gm Ir/SiO_2	17100	720

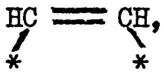
Table 42

catalyst	turning point of ^{14}CO adsorption isotherm (counts/min.)			
catalyst	on freshly reduced catalyst in the absence of acetylene	on freshly reduced catalyst in the presence of 12.5 torr acetylene in the gas phase	on catalyst in the steady state in the absence of acetylene	on catalyst in the steady state in the presence of 12.5 torr acetylene in the gas phase
0.2g Rh/SiO_2	11100	685	655	645
0.1g Pd/SiO_2	4050	320	2420	300
0.51g Ir/SiO_2	17100	720	650	630

Whilst the reasons for this are not readily apparent, it would appear that the presence of preadsorbed hydrogen in some way acts as a poison for the formation of the dissociatively adsorbed primary species.

4.2 ^{14}C - acetylene secondary adsorption isotherm:

The nature of the adsorbed species on the ^{14}C - acetylene secondary region was examined (section 3.2) indirectly by analysing the gas phase in equilibrium with the surface of freshly reduced Rh/SiO_2, Ir/SiO_2, Pd/SiO_2 and Pd/Al_2O_3 catalysts. It was found that the gas phase in equilibrium with the secondary region consist entirely of acetylene. Similar experiments conducted using catalysts in their steady states showed that the gas phase in equilibrium with the surface consisted entirely of acetylene. These experimental results are consistent with the assumption that the species on the secondary region are associatively adsorbed.

This assumption is in agreement with the suggestion of Rooney and Webb (144) that with alkynes and alkene the π - adsorbed species is the catalytically active species in hydrogenation reaction. This assumption also in agreement with the fact that di - σ - bonded complex, i.e.  $\underset{*}{HC}\equiv\underset{*}{CH}$, often observed in IR work (121).

The secondary adsorbed species arise from the adsorption of amounts of hydrocarbon in excess of that required for monolayer coverage. Indeed from the adsorption isotherms it can be deduced that, for example, at a gas pressure of 5 torr of acetylene, the ratio of the adsorbed acetylene to the total number of metal atoms is in excess of unity (1.02 for Pd/SiO_2, 1.12 for Ir/SiO_2 and 1.17 for Rh/SiO_s). This suggests that the secondary adsorption arises either from spill-over of the hydrocarbon onto the support as suggested by Reid et al (42, 43), or, involves the formation of overlayers on the metal surface (153). The latter idea is supported by the experimental results in section 3.8.3, which show that, using Rh/silylated SiO_2 in which all the - OH groups on the support are replaced by $Si(CH_3)_3$, the ^{14}C - acetylene adsorption isotherms are exactly similar to those obtained with an untreated Rh/SiO_2 catalyst, both in shape and in magnitude. Since, as noted by Lèvy and Boudart (154), the phenomenon of "spill-over" requires suitable sites on the support, it seems unlikely that the present observations can be satisfactorily interpreted in terms of "spill-over". The observation that the secondary adsorbed acetylene would not undergo molecular exchange with gaseous acetylene, nor could it be removed by evacuation (Tables 32, 33 and 34) shows that the adsorption was effectively irreversible. This conclusion is in agreement with those drawn for acetylene adsorption from studies of acetylene - deuterium exchange (137).

The effects of hydrogen on ^{14}C - acetylene species adsorbed on catalysts in their steady states are shown in figures 42 - 44. With each catalyst there is a rapid initial removal of secondary adsorbed species, followed by a further slow decrease in the surface count rate. The decrease in count rate in the rapid stage is independent of initial surface concentration of the secondary adsorbed acetylenic species, as shown in Tables 32 - 34, suggesting that only a constant number of the surface species are active towards hydrogen.

4.3 The relation between the catalytic activity and acetylene primary and secondary adsorption isotherms:

The experimental results in chapter 3 show that in the case of Rh/SiO_2 and Ir/SiO_2 catalysts the effect of deactivation by self poisoning reduces the extent of the ^{14}C - acetylene primary region by the progressive build up of permanently retained acetylenic species on the primary region until it disappears completely as the steady state activity is reached, that is, the amount of adsorbed acetylene which can be removed during the hydrogenation reaction and the subsequent treatment in hydrogen at ambient temperature progressively decreased from reaction to reaction.

Figures 12 and 20 show that the plot of the turning point of the primary region against the catalytic activity during the process of deactivation producesa straight line.

With Pd/SiO_2 and Pd/Al_2O_3 the effect of the deactivation was to reduce considerably the extent of ^{14}C - acetylene primary region. The deactivation has no observable effect on the secondary region. With freshly reduced Rh/SiO_2, Ir/SiO_2 and Pd/SiO_2, selective use of ^{14}C - tracer (section 3.2) shows that ^{14}C - acetylene primary region gives only ethane during hydrogenation and that over each of the catalysts, the acetylene adsorbed on the primary region showed, under reaction conditions, a much lower reactivity towards hydrogen than the secondary adsorbed acetylene. Using freshly reduced Rh/SiO_2, Ir/SiO_2 and Pd/SiO_2 the experimental results in section 3.2 show that, by covering the primary region with non-radioactive acetylene and the secondary region with ^{14}C - acetylene, during hydrogenation the secondary region gives a mixture of ^{14}C - ethylene and ^{14}C - ethane. The values of selectivities, S'', $S'' = \frac{^{14}C\text{-ethylene}}{^{14}C\text{-ethylene} + {}^{14}C\text{-ethane}}$, were equal to the values of the selectivities obtained using catalysts in their steady states.

The results of Chapter 3 show that, as the catalysts become progressively deactivated, the fraction of the primary adsorbed acetylene which can be removed by hydrogen at ambient temperature decreases, although during the deactivation the selectivity is observed to remain nearly constant (Tables 1,2,3 and 37). This confirms the lack of participation of the primary adsorbed acetylene in the hydrogenation reaction, since the selectivity remains constant, whereas it would be expected to increase if, on the freshly reduced catalysts, primary acetylene participated in the hydrogenation reaction.

From the discussion in this section and in section 4.2, it is apparent that at least three types of adsorbed acetylene can be recognised. Acetylene which participates in the hydrogenation reaction, located on the secondary region; acetylene which does not participate in the hydrogenation reaction but which can be removed by prolonged treatment in hydrogen and permanently retained acetylene, these latter two being located on the primary adsorption region.

4.4 The adsorption of carbon monoxide and effects of adsorbed carbon monoxide on acetylene hydrogenation:

The adsorption of ^{14}C - carbon monoxide was investigated using silica-supported rhodium, palladium and iridium catalysts under similar conditions to those used for acetylene hydrogenation. From the results shown in section 3.7 it can be seen that the ^{14}C - carbon monoxide adsorption isotherms on freshly reduced catalysts were of the form expected for Langmuir - type adsorption, consisting of a substantial non - linear primary region, without a secondary region. Figures 10, 15 and 18 show a comparison between the ^{14}C - carbon monoxide, ^{14}C - ethylene and ^{14}C - acetylene adsorption isotherm over freshly reduced rhodium, palladium and iridium catalysts respectively.

The ^{14}C - carbon monoxide adsorption isotherm using freshly reduced catalysts in the presence of 12.5 torr acetylene in the gas phase have a similar shape to those obtained on the clean surface, except that the total amount of ^{14}C - carbon monoxide adsorbed was substantially less; only approximately $\leqslant$ 8% of that adsorbed on the freshly reduced catalysts in the absence of acetylene, as shown in Table 42. Table 42 also shows that on steady state catalysts the amounts of ^{14}C - carbon monoxide was substantially less (5.9% Rh/SiO_2, 60% Pd/SiO_2 and 3.8% Ir/SiO_2) than on the clean freshly reduced catalysts.

Admission of 12.5 torr acetylene to a ^{14}C - carbon monoxide precovered freshly reduced catalysts resulted in a displacement of 29% (Rh/SiO_2), 37% (Pd/SiO_2) or 7% (Ir/SiO_2) of the carbon monoxide from the surface (Table 35). However with steady state catalysts, no displacement of carbon monoxide by acetylene was observed. These observations are consistent with the postulate that the primary adsorbed acetylene and carbon monoxide are both adsorbed directly on the metal, and that the acetylene is more strongly adsorbed than the fraction of carbon monoxide displaced. With silica - supported rhodium and iridium catalysts the amounts of ^{14}C - carbon monoxide adsorbed by the catalysts in their steady states was the same in the absence or presence of 12.5 torr acetylene in the gas phase, $\leqslant$ 6% of that amount adsorbed by the freshly reduced catalysts in the absence of acetylene. It is envisaged that this amount corresponds to the number of sites left vacant on the metal surface following monolayer coverage of the metal by adsorbed acetylenic species. With palladium - silica catalysts, however, whereas with a steady state catalyst in the absence of acetylene the amount of ^{14}C - carbon monoxide was only 60% that of the freshly reduced surface, the presence of 12.5 torr of acetylene in the gas phase reduced this amount to only 7% that of the freshly reduced catalyst. This latter observation is consistent with the earlier observation that, with the palladium catalyst, a substantial part of the primary adsorption region was regeneratable with hydrogen at ambient temperature, and with the postulate that, on the primary region, the acetylene is more strongly adsorbed than the carbon monoxide.

It is notable that, with each of the catalysts, the presence of 5 torr of carbon monoxide in the gas phase had <u>no effect</u> at all upon the acetylene secondary adsorption.

Experiments, described in section 3.7 show that the presence of 1 torr carbon monoxide in the acetylene - hydrogen reaction mixture resulted in the complete poisoning of the silica - supported rhodium and iridium catalysts both in the freshly reduced and steady states, although with palladium - silica only a partial reduction in hydrogenation activity resulted.

As discussed above, the adsorbed species responsible for the formation of the products in the hydrogenation reaction are located on the secondary region, and these appear to be unaffected by the presence of carbon monoxide. Furthermore, it has also been concluded that acetylene can effectively compete with carbon monoxide on the primary adsorption region, that is the actual metal surface. Together, these observations lead to the conclusion that the poisoning effects of carbon monoxide upon the acetylene hydrogenation cannot be simply described in term of a hydrocarbon "site - blocking" effect and an alternative explanation in terms of the effects of the carbon monoxide upon the surface concentration of the other reactant, namely hydrogen, must be sought. This will be discussed in detail in section 4.6 when the mechanism of the acetylene hydrogenation is discussed.

4.5 The concept of selectivity and the competition between ethylene and acetylene during hydrogenation:

It has been generally accepted (125, 126, 127) that in the selective hydrogenation of acetylene a thermodynamic factor is operative and that acetylene and ethylene compete for the same surface adsorption sites during hydrogenation of the former. The shapes of the pressure - time curves, together with the observation that the selectivity remains constant or nearly so until the acceleration point is reached has been taken to indicate that the thermodynamic factor is high. Consequently the presence of acetylene effectively prevents the readsorption of ethylene from the gas phase and also aids the desorption of ethylene. However, such conclusions make the implicit assumption that the same sites are involved in both acetylene and ethylene adsorption.

In a recent study of the hydrogenation of acetylene in the presence of excess ethylene over palladium - alumina catalysts (155), it has been suggested that at least two types of site exist on the catalyst surface. On type X sites the hydrogenation of both acetylene and ethylene can occur, although acetylene is adsorbed some 2200 times stronger than ethylene at 20°C. Type Y sites can hydrogenate ethylene in the presence of acetylene, but are inactive for hydrogenation of acetylene.

Results obtained in the present work also provide evidence for the existence of separate acetylene and ethylene adsorption sites. Thus admission of acetylene to the ^{14}C - ethylene pre-covered surfaces results in only a small decrease in the surface count rate; this amount being independent of the extent of the secondary region (Tables 32, 33 and 34).

On palladium and iridium surfaces the extent of ^{14}C - ethylene adsorption is independent of the presence or absence of acetylene in the gas phase. With rhodium the presence of acetylene in the gas phase results in a 30% decrease in ^{14}C - ethylene adsorption capacity of the surface, (Figures 39, 40, 41). From the quantities of the secondary adsorption isotherms the relative amounts of ethylene and acetylene ($^{n}C_2H_4/^{n}C_2H_2$) adsorbed under acetylene hydrogenation conditions at 298 K are 0.45 (Pd); 1.17 (Rh) and 0.78 (Ir).

Addition of ^{14}C - ethylene to the acetylene hydrogenation causes an increase in ethane yield. This increase, as determined from the amounts of ^{14}C - ethane produced, is directly proportional to the amount of added ethylene. Figures 33, 36 and 38 show that the plot of the amounts of ^{14}C - ethane formed against % conversion yields a straight line passing through the origin. It is, therefore, concluded that the hydrogenation of ^{14}C - ethylene proceeds independently of the amount of acetylene in the gas phase.

Collectively, these results lead to the conclusion that the adsorption and the hydrogenation of acetylene and ethylene occur on <u>independent</u> sites. Consequently, the observed selectivity will depend upon the relative concentration of the different types of surface site rather that upon the different strengths of adsorption of acetylene and ethylene, although such factors as the variation in availability of surface hydrogen with different hydrocarbon adsorbates (144), and the amounts of ethane formed directly from acetylene, not involving the formation of ethylene as an intermediate, must also be taken into account.

4.6 The mechanism of acetylene hydrogenation and the deactivation phenomena:

It has generally been postulated that the heterogeneously catalysed hydrogenation of unsaturated hydrocarbons proceeds by direct addition of hydrogen to adsorbed unsaturated hydrocarbon or to fragments of adsorbe unsaturated hydrocarbon. Bond and Wells (128) have proposed three types of mechanism for acetylene hydrogenation over alumina supported group V111 metals and nickel, in which they consider that hydrogenation should be regarded as hydrogen addition direct to adsorbed acetylene or to fragments of adsorbed acetylene. As an example: Bond, Webb and Wells (129) proposed the following mechanism to occur with Ru, Os, Ir and Rh:

With these metals the occurence of hydrogen exchange shows that hydrogen adsorption is reversible.

It was suggested that the rate determining step is probably the addition of hydrogen to an adsorbed vinyl species. The following mechanism is consistent with the experimental observations:

$$H_2\ (g) \rightleftharpoons 2H\ (a) \tag{1, 2}$$

$$C_2H_2\ (g) \longrightarrow C_2H_2\ (a) \tag{3}$$

$$C_2H_2\ (a) + H\ (a) \rightleftharpoons C_2H_3\ (a) \tag{4, 5}$$

$$C_2H_3\ (a) + H\ (a) \longrightarrow C_2H_4\ (a) \tag{6}$$

$$C_2H_4\ (a) \longrightarrow C_2H_4\ (g) \tag{7}$$

steady state analysis shows that:

$$\theta_{C_2H_3} = k_4\ \theta_{C_2H_2}\ \theta_{H}/(k_5 + k_6\theta_{H})$$

and the rate of ethylene production, V , is given by

$$V = k_4k_6\ \theta_{C_2H_2}\ \theta_{H}^{2} / (k_5 + k_6\theta_{H})$$

$$\theta_{C_2H_2} \longrightarrow 1 \text{ and } \theta_{H} \propto P_{H}^{0.5}$$

$$k_5 \gg k_6 \; \theta_H$$

$$\text{Thus} \quad V = \left(\frac{k_4 \, k_6}{k_5} \right) \; \theta_{C_2H_2} \, \theta_H^2$$

The observed order of unity in hydrogen is thus accommodated.

Thomson and Webb (139) recently proposed an alternative mechanism for catalytic hydrogenation of unsaturated hydrocarbons in which, as discussed in section 1.9, they suggested that hydrogenation should not be considered to occur by direct addition of a H - atom to an adsorbed hydrocarbon species, but rather through a hydrogen transfer between an adsorbed hydrocarbon species, M - C_xH_y, which is permanently retained on the catalyst surface, and associatively adsorbed unsaturated hydrocarbon. The experimental results reported in this thesis provide additional evidence for these proposals.

According to the theory of direct H - addition the self - poisoning must be caused either by poisoning hydrogen adsorption sites or by poisoning the sites on which the conversion of adsorbed acetylene to the products takes place; neither self - poisoning or carbon monoxide poisoning appear to affect the surface concentration of the catalytically active adsorbed acetylene as discussed above. The results of the present work are not inconsistent with the above two possibilities. The experimental results in section 3.7 and the discussion in section 4.4 show, by using ^{14}C - carbon monoxide as a probe, that it can be assumed that there are active sites, located on the metal, which may be considered to be responsible for hydrogen adsorption. It follows from the ^{14}C - carbon monoxide adsorption studies that the process of self - poisoning cannot be ascribed to the loss of these sites, since the amounts of carbon monoxide adsorbed on freshly reduced and steady state catalysts in the presence of gas phase acetylene are virtually identical. Thus, the number of hydrogen adsorption sites on the steady state catalysts, expressed as a percentage of the number of such sites on a freshly reduced catalyst are 98% (Rh/SiO_2), 92% (Pd/SiO_2) and 88% (Ir/SiO_2) (Table 42). These values contrast sharply with the percentage decreases in catalytic activity from freshly reduced to steady state catalysts, which are 97.7% (Rh/SiO_2) 89% (Pd/SiO_2) and 96.8% (Ir/SiO_2). Clearly, assuming the validity of identity of the carbon monoxide and hydrogen adsorption sites on each catalyst under hydrogenation conditions, the self - poisoning phenomena, resulting in the deactivation of the catalysts, cannot be ascribed to blocking of the hydrogen adsorption sites.

Trow the present results the existence of at least three types of surface site can be deduced. These are as follows:

(1) Sites located on the metal on which carbon monoxide may be adsorbed in the presence of acetylene. Trow a comparison of the amounts of carbon monoxide adsorbed on freshly reduced and steady state catalysts it is envisaged that these sites may be identified as "holes" in the fully covered acetylene primary adsorption region which arise due to the geometrical restrictions imposed in the adsorption of the latter. From the poisoning effects of adsorbed carbon monoxide upon acetylene hydrogenation it has also been concluded that these sites are also available for the non - competitive adsorption of hydrogen during acetylene hydrogenation.

(2) Sites located on the secondary region which are responsible for the adsorption of acetylene in a catalytically active form,

that is, the actual acetylene molecules which undergo catalytic "turnover" to products. These sites are not affected to any appreciable extent either by the process of deactivation or by the presence of carbon monoxide.

(3) Sites located on the acetylene primary region, considered to be the actual metal surface, on which the acetylene is present predominantly as dissociatively adsorbed species and, possibly as a polymeric species. If, as the results suggest, species of the type $M - C_2H_x$ ($x \leqslant 2$) occur on the primary adsorption region, then, following the proposals of Thomson and Webb (139) the process of deactivation, acetylene hydrogenation and the poisoning effect of carbon monoxide are explicable as discussed below.

Representing the hydrogen transfer complex, located on the primary region as $M - C_2H_x$, (its precise chemical identity has yet to be established), and considering that hydrogenation proceeds through the tranfer of hydrogen from the hydrogenated $M - C_2H_x$ species to associatively adsorbed acetylene, located on the secondary region, the following mechanism for acetylene hydrogenation can be written;

$$H_2\,(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{matrix}H_2\\ \vdots\\ *\end{matrix} \tag{1, 2}$$

$$\begin{matrix}H_2\\ \vdots\\ *\end{matrix} + M - C_2H_x \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \begin{matrix}H\\ |\\ *\end{matrix} + M - C_2H_{x+1} \tag{3, 4}$$

$$\begin{matrix}H\\ |\\ *\end{matrix} + M - C_2H_x \underset{k_6}{\overset{k_5}{\rightleftharpoons}} M - C_2H_{x+1} \tag{5,6}$$

$$M - C_2H_{x+1} + C_2H_2\,(a) \underset{k_8}{\overset{k_7}{\rightleftharpoons}} M - C_2H_x + C_2H_3\,(a) \tag{7,8}$$

$$C_2H_3\ (a) + \overset{H}{\underset{*}{\downarrow}} \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} C_2H_4\ (a)$$

$$C_2H_3\ (a) + M - C_2H_{x+1} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} C_2H_4\ (a) + M - C_2H_x$$

$$C_2H_4\ (a) \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} C_2H_4\ (g)$$

Steady state analysis of this reaction mechanism can be carried out as follows:

Rate of formation of $\overset{H_2}{\underset{*}{\vdots}}$ = Rate of disappearance of $\overset{H}{\underset{*}{\vdots}}$

$$k_1 P_{H_2} (1 - \theta_{H_2}) + k_4 \theta_H \theta_{C_2H_{x+1}} = k_3 \theta_{H_2} \theta_{C_2H_x} + k_2 \theta_{H_2} \qquad (1)$$

let $(1 - \theta_{H_2}) \approx 1$ (hydrogen is weakly adsorbed)

let $k_1 P_{H_2} (1 - \theta_{H_2}) \gg k_4 \theta_H \theta_{C_2H_{x+1}}$

and $k_2 \theta_H \gg k_3 \theta_{H_2} \theta_{C_2H_x}$ then equation no. 1 become:

$$k_1 P_{H_2} = k_2 \theta_{H_2} \quad \therefore \quad \theta_{H_2} = \frac{k_1}{k_2} P_{H_2} \qquad (2)$$

Rate of formation of $\overset{H}{\underset{*}{\downarrow}}$ = Rate of disappearance of $\overset{H}{\underset{*}{|}}$

$$k_3 \theta_{H_2} \theta_{C_2H_x} + k_{10} \theta_{C_2H_4} + k_6 \theta_{C_2H_{x+1}}$$

$$= k_5 \theta_H \theta_{C_2H_x} + k_9 \theta_H \theta_{C_2H_3} \qquad (3)$$

assuming that $k_3 \theta_{H_2} \theta_{C_2H_x} \gg k_{10} \theta_{C_2H_4} + k_6 \theta_{C_2H_{x+1}}$

and $k_5 \theta_H \theta_{C_2H_x} \gg k_9 \theta_H \theta_{C_2H_3}$ (hydrogenation cannot proceed by a direct addition of hydrogen to adsorbed unsaturated hydrocarbon or to an adsorbed fragment of unsaturated hydrocarbon)

Then equation 3 becomes:

$$k_3 \theta_{H_2} \theta_{C_2H_x} = k_5 \theta_H \theta_{C_2H_x}$$

$$\theta_H = \frac{k_3}{k_5} \theta_{H_2} \qquad (4)$$

from equation (4) and (2)

$$\theta_H = \frac{k_3 k_1}{k_5 k_2} P_{H_2} \tag{5}$$

Rate of formation of $M - C_2H_{x+1}$ = Rate of removal of $M - C_2H_{x+1}$

$$k_3 \theta_{H_2} \theta_{C_2H_x} + k_5 \theta_H \theta_{C_2H_x} + k_8 \theta_{C_2H_x} \theta_{C_2H_3} + k_{12} \theta_{C_2H_4} \theta_{C_2H_x}$$

$$= k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} + k_4 \theta_H \theta_{C_2H_{x+1}} + k_6 \theta_{C_2H_{x+1}} + k_{11} \theta_{C_2H_3} \theta_{C_2H_{x+1}} \tag{6}$$

assuming that:

$$k_3 \theta_{H_2} \theta_{C_2H_x} + k_5 \theta_H \theta_{C_2H_x} \gg k_8 \theta_{C_2H_x} \theta_{C_2H_3} + k_{12} \theta_{C_2H_4} \theta_{C_2H_x}$$

and that

$$k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} + k_{11} \theta_{C_2H_3} \theta_{C_2H_{x+1}} \gg k_4 \theta_H \theta_{C_2H_{x+1}} + k_6 \theta_{C_2H_{x+1}}$$

equation 6 becomes:

$$k_3 \theta_{H_2} \theta_{C_2H_x} + k_5 \theta_H \theta_{C_2H_x}$$

$$= k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} + k_{11} \theta_{C_2H_3} \theta_{C_2H_{x+1}}$$

$$\frac{k_3 k_1}{k_2} P_{H_2} \theta_{C_2H_x} + \frac{k_5 k_3 k_1}{k_5 k_2} P_{H_2} \theta_{C_2H_x}$$

$$= (k_7 \theta_{C_2H_2} + k_{11} \theta_{C_2H_3}) \theta_{C_2H_{x+1}}$$

$$\theta_{C_2H_{x+1}} = \frac{2k_3 k_1}{k_2} \frac{P_{H_2} \theta_{C_2H_x}}{(k_7 \theta_{C_2H_2} + k_{11} \theta_{C_2H_3})} \tag{7}$$

Rate of formation of C_2H_3 (a) = Rate of removal of C_2H_3 (a)

$$k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} + k_{12} \theta_{C_2H_4} \theta_{C_2H_x}$$

$$= k_9 \theta_H \theta_{C_2H_3} + k_{11} \theta_{C_2H_3} \theta_{C_2H_{x+1}} + k_8 \theta_{C_2H_x} \theta_{C_2H_3} \tag{8}$$

if $k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} \gg k_{12} \theta_{C_2H_4} \theta_{C_2H_x}$

and $k_{11} \theta_{C_2H_3} \theta_{C_2H_{x+1}} \gg k_9 \theta_H \theta_{C_2H_3} + k_8 \theta_{C_2H_x} \theta_{C_2H_3}$

equation (8) becomes:

$$k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} = k_{11} \theta_{C_2H_3} \theta_{C_2H_{x+1}}$$

$$\therefore \theta_{C_2H_3} = \frac{k_7}{k_{11}} \theta_{C_2H_2} \qquad (9)$$

From equations (9) and (7)

$$\theta_{C_2H_{x+1}} = \frac{2k_3k_1}{k_2} \frac{P_{H_2}\theta_{C_2H_x}}{k_7\theta_{C_2H_2} + k_{11}\frac{k_7}{k_{11}}\theta_{C_2H_2}}$$

$$\theta_{C_2H_{x+1}} = \frac{k_3k_1}{k_2k_7} \frac{P_{H_2}\theta_{C_2H_x}}{\theta_{C_2H_2}} \qquad (10)$$

Considering the rate determining step to be step (7):

$$\text{reaction rate} = V = k_7 \theta_{C_2H_{x+1}} \theta_{C_2H_2} \qquad (11)$$

which from 10 and 11 becomes:

$$V = \frac{k_3k_1}{k_2} \theta_{C_2H_x} P_{H_2} \qquad (12)$$

equation (12) shows that the rate of the reaction is directly proportional to the concentration of the hydrogen transfer active centre, M - C_2H_x, and that the reaction is first order with respect to H_2.

The process of deactivation, in which the amounts of the acetylene adsorbed on the primary region, which can be removed by treatment with hydrogen at the reaction temperature, progressively decreases, may also be explained in terms of the hydrogen - transfer mechanism by considering that in the deactivation process the concentration of M - C_2H_x active centres progressively diminishes. Processes which could account for this decrease are (a) sintering of the metal during hydrogenation, as observed previously with palladium/graphite catalysts (156); (b) further dehydrogenation of the C_2H_x species leading to the formation of surface carbide and (c) the effective removal of the C_2H_x through its participation in a surface hydropolymerisation reaction. The observation that complete regeneration of the catalytic activity could be achieved for each catalyst by heating in hydrogen to 623 K, and that effective deactivation requires the presence of hydrogen suggest that the surface hydropolymerisation reaction is the most likely cause of the deactivation.

It is envisaged that in the steady state a small number of stable $M - C_2H_x$ species remain on each catalyst surface, this steady state concentration of $M - C_2H_x$ giving rise to the constant activity observed with each catalyst at a particular temperature. Thus the specific activity of a particular catalyst will depend upon its ability to stabilize the surface $M - C_2H_x$ surface complex. In this context it is interesting to note that palladium, which showed a small primary region even in the steady state, was observed to possess an appreciably higher steady state activity than rhodium or iridium, which both showed virtually no primary region in the steady state.

The concept of the formation of $M - C_2H_x$ active centres on the catalyst surface also provides an explanation of the poisoning effect of carbon monoxide upon the acetylene hydrogenation. This may be achieved by considering that on acetylene precovered surface the carbon monoxide either blocks the site at which the molecular hydrogen is adsorbed before reacting with the $M - C_2H_x$ centre or it reacts with the adsorbed C_2H_x hydrocarbon residue. Blyholder (157) has observed reaction between adsorbed hydrocarbon and carbon monoxide.

4.7 Overall Conclusions:

From the results presented in this thesis two interesting and important features emerge regarding the catalytic hydrogenation of acetylene. First the results are most satisfactorlly interpreted by a mechanism involving hydrogen transfer between a dissociatively adsorbed C_2H_x species and associatively adsorbed acetylene, which forms an overlayer on the dissociatively adsorbed acetylene. The permanent retention of acetylenic species is suggested as being due to surface polymer formation.

The second feature emerges from the studies of the co - adsorption of ethylene and acetylene. These show that under acetylene hydrogenation conditions, they are adsorbed at separate sites and undergo hydrogenation independently of each other.

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