Radiochemical Methods in the Study of Platinum Metal Catalysis

A REVIEW OF RECENT APPLICATIONS

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Because of their extreme sensitivity, radiochemical methods are of great help in the study of catalytic processes. Changes at a surface at concentrations less than those required to yield monolayer coverage can readily be detected without interrupting the system for analysis. This article describes the application of such methods to the determination of metal areas and of catalytically active areas in supported metal catalysts and also reviews their usefulness in the study of electrocatalysis and in the unravelling of catalytic reaction mechanisms.

Radioactivity takes its place among the major methods of studying surface processes because of its sensitivity of detection. This is illustrated if we consider changes at the surface of a typical platinum metal: this exposes approximately 10^{15} atoms per square centimetre and it will chemisorb about half that number of diatomic molecules. Thus changes in or at the surface involve $\sim 10^{-8}$ moles per square centimetre, an amount difficult to detect by ordinary chemical means. However, if the adsorbate molecules or surface atoms are made radioactive, then changes at the surface are readily detectable. For example, if the radioactive concentration of an adsorbed species is 1 millicurie per millimole, then with a detector of 10 per cent efficiency viewing the surface, the appearance of a monolayer at the surface would change the count rate from 30 c.p.m. (background) to 230 c.p.m.

The implication of the above figures is that, at concentrations less than those required to yield monolayer coverage, changes at a surface can be detected without interrupting the system for analysis. The technique has been exploited in catalyst poisoning studies, in studies of the displacement of one adsorbed species by another, and in studies of surface heterogeneity. In the present article the potentialities of this approach to surface chemistry and catalysis are illustrated by reference to specific examples.

Surface Area Measurements

In evaluating supported-metal catalysts, one parameter which is required is the area of exposed metal surface. Conventional BET measurements are unsatisfactory as these are non-selective and yield the total (support + metal) area. Metal areas of supported-platinum metal catalysts can be accurately determined by the adsorption of ^{14}C-carbon monoxide. In one such study, Hughes *et al.* (1) determined metal areas for Pt-Al$_2$O$_3$ and Rh–Al$_2$O$_3$ catalysts by the adsorption of ^{14}CO in a flow system using helium as carrier gas. The precision of the method is good. For two-gramme samples of an 0.4 per cent Pt–Al$_2$O$_3$ reforming catalyst, the standard deviation was 0.40 μmole.g^{-1}. Several other interesting observations were made in this study. Below 310°C reduction of catalysts was incomplete, while between 400 and
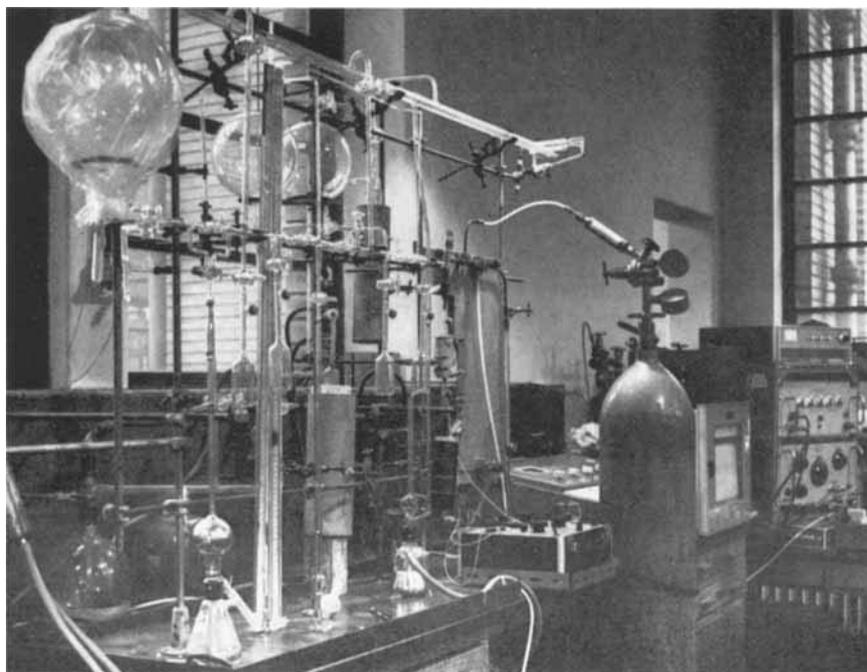
Microcatalytic reactor for the study of the adsorption of ^{14}C- and ^3H- labelled compounds on supported-metal catalysts. The products are examined in a chromatograph and in a gas-proportional counter
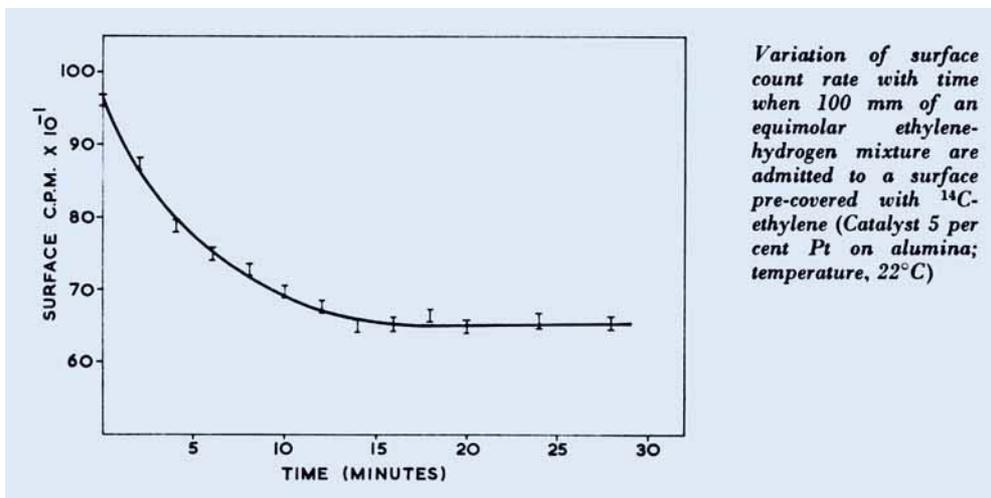
600°C the amount of ^{14}CO adsorption decreased due to sintering of the metal. The amount of ^{14}CO adsorbed was the same, within 0.5 per cent, when the catalyst was cooled in hydrogen or when flushed with helium at high temperature. This suggests that carbon monoxide and hydrogen are adsorbed on different types of site. It was also found that CO chemisorption was proportional to platinum content over a hundredfold variation in metal content. Thus under the conditions used, metal-particle size was independent of metal content.

Chemisorption and Catalysis

The ultimate requirement in a comparison of catalysts, both from the theoretical and practical viewpoints, lies in comparison of the catalyst activities per *unit area*. In this context unit area is used in the strictest sense to mean unit area of surface *active in catalysis*.

Such measurements have been made for evaporated metal films and supported-metal catalysts by a technique devised by Thomson, Cormack, Webb and Wishlade (2, 3). ^{14}C-ethylene was adsorbed on the catalyst surface, the uptake being followed directly by a Geiger-Müller counter mounted inside the catalyst vessel and monitoring the catalyst surface. Inactive ethylene/hydrogen mixtures were then admitted to the labelled surface and the hydrogenation reaction was followed manometrically. Simultaneously, the fall in surface radioactivity was observed by the Geiger-Müller counter, as shown in the graph on page 48. From the results it is at once apparent that only a fraction of the initially adsorbed ^{14}C-ethylene is involved in subsequent hydrogenation. The percentages of initially adsorbed material retained on various alumina-supported metal catalysts (supplied by Johnson Matthey) at 25°C were as follows: Pd 63.5 per cent, Rh 22.5 per cent, Ir 16.0 per cent, Pt 6.5 per cent. Similar retentions were observed when the labelled surface was allowed to undergo molecular exchange with inactive ethylene in the absence of hydrogen.

Variation of surface count rate with time when 100 mm of an equimolar ethylene-hydrogen mixture are admitted to a surface pre-covered with ^{14}C-ethylene (Catalyst 5 per cent Pt on alumina; temperature, 22°C)

The relationship between chemisorption and catalysis has also been investigated by Klier and Kuchynka (4) using the radio-chemical approach. In a study of the Pt–MnO$_2$-catalysed oxidation of carbon monoxide between —78°C and 20°C, these workers have investigated the nature and reactivity of surface species, namely CO and CO$_2$. ^{14}CO was adsorbed on the catalyst surface and the labelled surface was then treated with ^{12}CO and ^{12}CO$_2$. By monitoring the gas-phase activity the extent of the exchange reactions was determined.

Electrocatalysis

The determination of the concentration of surface species has a fundamental importance in electrode and electrocatalytic processes. Such studies are currently being undertaken because of the importance of the platinum metals in fuel cells.
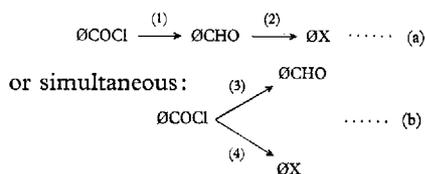
Mádi (5) has shown that for ^{144}Ce deposition on Pt, the Langmuir adsorption isotherm was applicable and the equilibrium coefficient varied with the Ce$_2$(SO$_4$)$_3$ concentration. The number of active sites for deposition was dependent upon the anode voltage and, at constant voltage, upon the temperature. ^{14}C-labelled hydrocarbons have been used to determine the surface concentrations during electrocatalytic oxidation and hydrogenation. Thus ^{14}C-ethylene

concentrations on platinum electrodes have been determined as a function of electrode potential and time, by studying the adsorption on platinum foils which are used to cover a proportional counter (6). Bockris *et al.* (7) have made similar measurements using ^{14}C-ethylene and metal films supported on the window of a Geiger-Müller tube detector.

Catalyst Poisoning and Mechanistic Studies

The application of radioactive tracer techniques to mechanistic studies is, in principle, the same as the application to homogeneous systems. This being so, we consider only one specific example.

The hydrogenation of benzoyl chloride over a Pd-BaSO$_4$ catalyst produces a variety of products such as benzaldehyde, benzyl alcohol, toluene and benzoic acid. By partially poisoning the catalyst with tetramethyl-thiourea, the selectivity for benzaldehyde formation can be greatly enhanced. In establishing the mechanism of the poisoning action it is necessary to know whether the reaction is consecutive,

$$\text{ØCOCl} \xrightarrow{(1)} \text{ØCHO} \xrightarrow{(2)} \text{ØX} \cdots\cdots \text{(a)}$$

or simultaneous:

$$\text{ØCOCl} \begin{array}{c} \xrightarrow{(3)} \text{ØCHO} \\[1ex] \xrightarrow{(4)} \text{ØX} \end{array} \cdots\cdots \text{(b)}$$

To distinguish between these two possibilities ^{14}C-benzaldehyde was added to the reaction mixture and its behaviour with time was followed by means of scintillation counting (8). As the reaction proceeded the ^{14}C-benzaldehyde concentration decreased, showing that the consecutive mechanism (a) was operative and that the poison affected step (2).

In another study using scintillation counting, the effect of catalyst poison on chemisorption has been investigated (9). The adsorption and hydrogenation of vinylacetic acid and crotonic acid, both ^{14}C-labelled, were studied first on an unpoisoned Pd-BaSO$_4$ catalyst, and then on a thiophen poisoned Pd-BaSO$_4$ catalyst. The results showed that, although the thiophen-poisoned catalyst was inactive for hydrogenation, the amount of adsorption was unaffected by the presence of poison. These were taken to indicate that while adsorption occurred generally on all surface sites, only a small fraction of the sites were active for hydrogenation. Only these latter sites were affected by the poison.

This heterogeneity of catalyst surfaces is easily detectable by tracer methods. For such studies a displacement method, in which Hg labelled with [197]Hg and [203]Hg displaces hydrogen and then tritium from metal films, has been devised (10). Thermal desorption of [203]Hg has also been used (11) to investigate the surface heterogeneity of an asbestos-supported platinum catalyst.

Labelled Surfaces

In the applications so far discussed the radioactive atoms have been incorporated in the adsorbate rather than in the adsorbent. However, labelled surfaces themselves may also be used. In a study of the reaction between hydrogen and oxygen over platinum, Jech (12) used a platinum sponge and a platinum foil, whose surface had been labelled with [85]Kr, [131]Xe or [222]Rn. The surface labelling was achieved by impelling the inert gas atoms into the surface as ions under a potential drop. The results of this study showed that radioactive gas was liberated from the surface

as the reaction proceeded. From the activities before and after reaction it was possible to show that only a fraction of the surface was catalytically active. The potentialities of this technique are large, since this method of surface-labelling is almost universal.

References

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The Selection and Use of Thermocouple Sheaths

Without adequate protection from the relatively few substances that can contaminate them, platinum thermocouples can deteriorate rapidly. Given such protection, in the form of a carefully chosen refractory sheath properly looked after, they will give long and reliable service at high temperatures often in apparently adverse conditions. The subject of sheath materials and design is a somewhat neglected one, and it is valuable to have available a survey of the variety of old and newer sheath materials that can be used in the many applications of thermocouples in metallurgical processes. D. W. Brown, of Morganite Research and Development, has provided such a review (*J. Inst. Metals,* 1967, **95**, 12–17), together with useful guidance on such important details as the size and positioning of sheaths in various types of furnaces and their careful handling in service.