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PULSE METHOD FOR THE RADIO-CHROMATOGRAPHIC DETERMINATION OF THE SORPTION CAPACITY OF CATALYSTS*

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SUMMARY

A radio-gas-chromatographic method is presented for determination of the quantities of components sorbed irreversibly on catalysts and adsorbents. The method is illustrated with measurements on the chemisorption of H_2/HT on Wilkinson's catalyst.

INTRODUCTION

In investigations of the mechanisms and kinetics of heterogeneous catalytic reactions, it is indispensable to study the adsorption properties of the catalyst including the extents to which the reactants are chemisorbed on the catalyst.

A number of methods are known for the determination of the adsorption capacities of solid or dissolved catalysts. In laboratories where the necessary equipment (volumetric adsorption apparatus, sorptometer, etc.) is not available, use can be made of the "pulse dynamic method" described by Paryjczak *et al.*^{1,2} which can be carried out on a normal gas chromatograph. Our method differs from this in using a radiation detector, a natural choice for the detection of labelled gas components, instead of a thermal conductivity detector, which was used by Paryjczak *et al.*

For application of the method, the radiograph itself is in fact sufficient; it is in essence a flow-proportional counter (supplemented with feed-gas supplies and electronic amplifying and recording units).

Description of method

The principle of the measurement is very simple. Impulses of known volumes of the gaseous or vapour-phase component labelled with 3H or ^{14}C are passed into

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the radiograph, and the count for one impulse is determined. Next, a reactor (or column) packed with a known amount of catalyst is connected in the path of the carrier gas (by means of a suitable valve), and impulses of the labelled component are passed, one after another, through the column into the detector, until the impulses are unchanged by passage through the catalyst (by comparison with the previously determined count). The difference in total activity, ascribable to the impulses admitted to the catalyst and the impulses measured, is proportional to the quantity of the component that is chemisorbed.

The method can be employed unambiguously only in the case of irreversible adsorption (chemisorption).

EXPERIMENTAL

Measurements were made on a radio gas chromatograph obtained by coupling a Perkin-Elmer RGC-170 radiograph and a Hewlett-Packard 5710 A gas chromatograph, with an appropriate gas-mixing apparatus and a gas-feed valve. The equipment is depicted in Fig. 1. An account of the theoretical and practical problems of radio-gas-chromatographic measurements involving a proportional counter as detector is to be found in ref. 3.

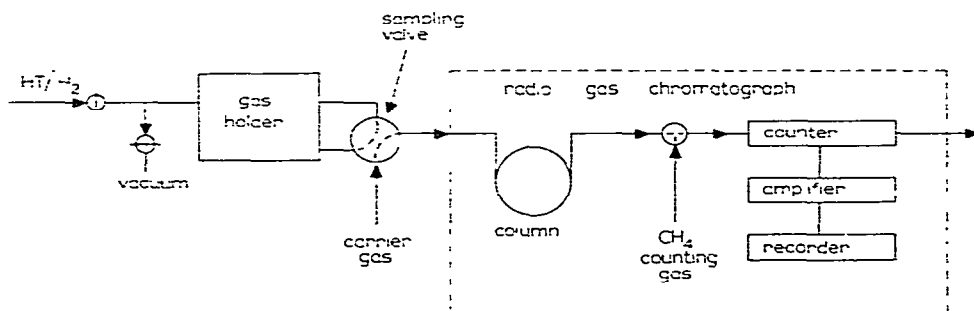


Fig. 1. Experimental apparatus.

Measurements were carried out with 3H -labelled dihydrogen, the specific activity of which had been adjusted to the desired value of $ca. 10^{12} \text{ Bq mol}^{-1}$ by dilution with inactive dihydrogen. At room temperature the volume (V) of the gas burette containing the labelled dihydrogen was 128.5 cm^3 . From this, gas impulses of volume $v = 0.5 \text{ cm}^3$ were added to the carrier gas going into the gas-chromatograph. The flow-rate of the nitrogen carrier gas was varied from 0.5 to $2.0 \text{ cm}^3 \text{ sec}^{-1}$.

The catalyst to be examined was packed into the column of the gas chromatograph. In the present measurements, a study was made of the hydrogen-binding capacity of Wilkinson's hydrogenation catalyst⁴; this consists of tris(triphenylphosphine)rhodium(I) chloride [$(\text{TPP})_3\text{RhCl}$] in 1,1-diphenylethylene on a solid support. Before the experiments, the catalyst charge was evacuated at 10^{-2} Pa for 30 min at 333°K . The packed column ($2 \text{ m} \times 3 \text{ mm}$) in the gas chromatograph was thermostatted to the desired value between 273 and 333°K .

The total activity of the tritiated dihydrogen impulse used in the measurements was determined before the measurements themselves. The impulses were led through

the empty column directly into the detector, and the numbers of counts per impulse were recorded. The activity of the β -emitting tritium was measured with a flow-proportional counter with a volume of 10.0 cm^3 , in which methane fed in at a flow-rate of $0.2\text{--}1.0 \text{ cm}^3 \text{ sec}^{-1}$ was used as counter gas.

During the actual measurement, labelled sorbate (tritiated dihydrogen) impulses were admitted at definite intervals onto the column containing the adsorbent (the catalyst) and the activities of the leaving impulses were detected. If the adsorption capacity of the catalyst is high, no leaving impulse is observed initially. However, when the amount of adsorbate irreversibly bound by the catalyst approaches the chemisorption capacity, increasingly greater gas impulses leave the column, and finally only impulses unchanged in magnitude, with the activity determined in the preliminary experiments, are observed.

A very important feature in the planning of the experiments is the suitable choice of the quantity of the adsorbent, or the catalyst to be studied (the charge of the column). If this is relatively large, very many impulses will be required for saturation to be attained, and the measurement may last an inconveniently long time. However, if the adsorption capacity of the column charge is small compared to the volume of the impulse, then the measurement will be completed within a few impulses; this is disadvantageous, for the statistical fluctuation in the detection of the radioactivity in the case of a small number of experimental points may cause a large error.

RESULTS

In order to show the capabilities of the method, the chemisorption of dihydrogen ($^3\text{H}_2$) was measured on a Wilkinson-type catalyst at 333°K . The column packing consisted of 15% (w/w) of a solution of $(\text{TPP})_3\text{RhCl}$ in 1,1-diphenylethane (17 mmol of the salt dissolved in 1 dm^3 solvent) on a Porolith support. From this column filling, 4.35 g was actually used. The first impulse contained $2.69 \cdot 10^{-7} \text{ mol H}_2$ and its total activity corresponded to $A_1^0 = 236,200$ counts.

The experimental results are summarized in Table I and Fig. 2. It is seen that the observed number of counts per pulse increases from the first to the seventh pulse, but decreases after the eighth. This is due to the decrease in the material content of the gas burette. It is obvious that, disregarding statistical fluctuations, the experimental points increasingly tend to lie on the line calculated from the volume ratio v/V . In the given case

$$v/V = \frac{0.50 \text{ (cm}^3\text{)}}{128.5 \text{ (cm}^3\text{)}} = 0.003891$$

Also, the amount of H_2 in each successive pulse is reduced by 0.3891%. Consequently the activities of the pulses can be computed from the equation

$$A_n^0 = A_1^0 (1 - v/V)^{n-1} \quad (n = 2, 3, \dots) \quad (1)$$

where n is the serial number of the given pulse. (The values A_n^0 are marked by + in Fig. 2.) It follows from the series expansion

TABLE I
EXPERIMENTAL RESULTS

Pulse number (n)	Count number; pulse				
	Measured	Calculated		Differences	
	(A_n)	A_n^0	A_n^*	$A_n^0 - A_n$	$A_n^* - A_n$
1	219300	236200	236200	16900	16900
2	226950	235281	235281	8331	8331
3	227700	234365	234362	6665	6662
4	228900	233454	233443	4554	4543
5	230100	232545	232524	2445	2424
6	230400	231640	231605	1240	1205
7	229650	230739	230686	1089	1036
8	230400	229841	229767	- 559	- 633
9	228900	228947	228848	47	- 52
10	227850	228056	227929	206	79
11	229200	227167	227010	- 2033	- 2190
12	224400	226285	226091	1885	1690
13	225750	225404	225172	- 346	- 578
14	224250	224527	224253	277	3
15	223200	223653	223334	453	134
16	-	222783	222415	-	-

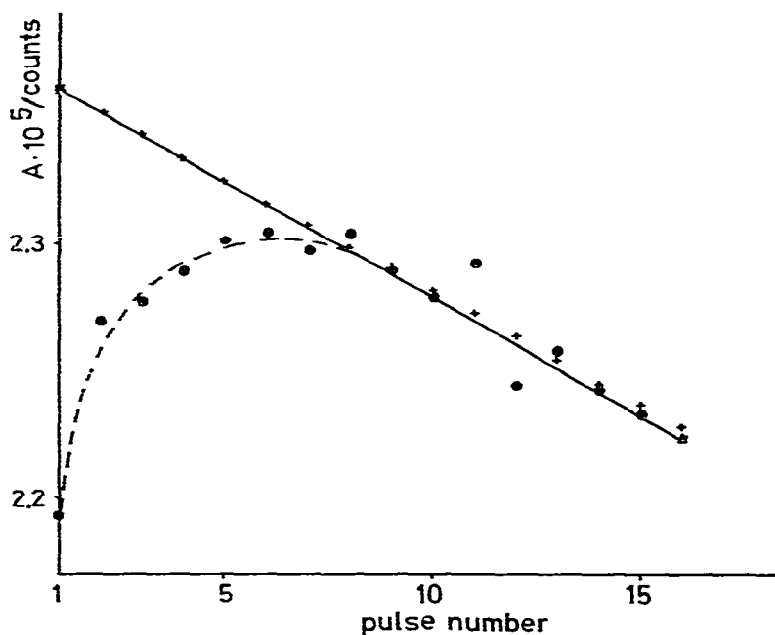


Fig. 2. Determination of the chemisorbed amount of hydrogen on a sample of Wilkinson's catalyst. Temperature: 333°K; flow-rate of the carrier gas: $2 \text{ cm}^3 \text{ sec}^{-1}$; material content of a pulse: $2.69 \cdot 10^{-7} \text{ mol H}_2$; ● = measured count number (A_n); + = calculated count number (A_n^0).

$$\frac{A_n^0}{A_1^0} = \sum_{i=0}^{n-1} \binom{n-1}{i} (-v/V)^i = 1 - (n-1)v/V + \frac{(n-1)(n-2)}{2} (v/V)^2 - \dots + (v/V)^{n-1}$$

that instead of eqn. 1 the simple relationship

$$A_n^0 = A_n^* = A_1^0 [1 - (n-1)v/V] \quad (2)$$

holds for the decrease in the activities of the successive pulses, provided v/V is sufficiently small. It is clearly seen from the Fig. 2 that the straight line (*) drawn according to eqn. 2 fits the points computed from eqn. 1 especially well at low counts per pulse.

For the application of the pulse dynamic method, provided nearly 10 pulses are sufficient to saturate the sorbent, no correction is necessary in the case of $v/V < 10^{-4}$ ($A_n^0 \equiv A_1^0$); the simple correction eqn. 2 is satisfactory if $10^{-4} < v/V < 10^{-2}$; in every other case the activities have to be corrected according to eqn. 1 if greater precision is needed.

The chemisorbed amount can be computed from the sum of the differences [counts (fed) - counts (observed)] for each pulse; finally this total count should be divided by the specific activity of dihydrogen (in the same units).

From Table I it follows that

$$\sum_{n=1}^7 (A_n^0 - A_n) = 41224; \quad \sum_{n=1}^7 (A_n^* - A_n) = 41101$$

$$\sum_{n=1}^{15} (A_n^0 - A_n) = 41154; \quad \sum_{n=1}^{15} (A_n^* - A_n) = 39555$$

In other words this means that in the given example the linear correction is completely satisfactory. This is more true if the sum is taken only up to that pulse where, in Fig. 2, the dashed curve reaches the straight line (seventh pulse).

From the specific activity $8.78 \cdot 10^{14}$ counts mol^{-1} H_2 of the dihydrogen (as computed from the first pulse), it follows that the chemisorbed amount of H_2 on the Wilkinson-type catalyst at 333°K corresponds to

$$\frac{41224 \text{ counts}}{4.35 \text{ g } 8.78 \cdot 10^{14} \text{ counts mol}^{-1} \text{ H}_2} = 1.079 \cdot 10^{-8} \text{ mol H}_2 \text{ g}^{-1}$$

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