Reversed Flow Gas Chromatography for studying Heterogeneous Catalysis

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Summary The rate constants of surface catalysed reactions can be determined in a gas chromatographic column, containing the catalyst, by repeatedly reversing the direction of flow of the carrier gas.

The detailed kinetics of surface catalysed reactions can with advantage be studied by the following technique. The catalyst is contained in a gas chromatographic column of total length $l' + l$ (Figure 1), and the reactant A is introduced as a pulse (*e.g.* a few mm³ of liquid using a microsyringe) at position $x = l'$, with the carrier gas flowing in the direction F (forward) to the flame ionisation detector at position D_1. If A is more strongly adsorbed than the product(s), the latter is recorded by the detector as an asymmetric elution curve. At a time (measured from the moment of injection) greater than the retention time t_R of the product B on the column length l, the direction of the carrier gas flow is *reversed*, and the detector is now placed at position D_2 by means of a four or six-port valve. The detector signal for B now appears approximately as a square function followed by a decaying curve (Figure 2, peak 1). After a time (from the moment of reversal) greater than the total retention time $t_R + t'_R$ of B on the total column length $l + l'$, the carrier gas flow is again turned to the direction F. Following this, a new square signal is recorded by the detector (Figure 2, peak 2). This procedure is repeated several times, until two series of peaks are obtained. One with the carrier gas

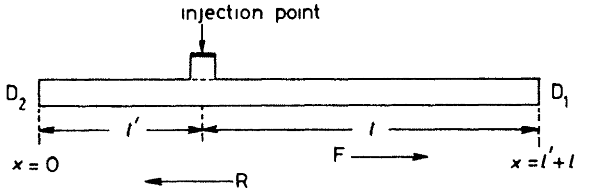

Figure 1. Schematic representation of the chromatographic column in the reversed flow method.

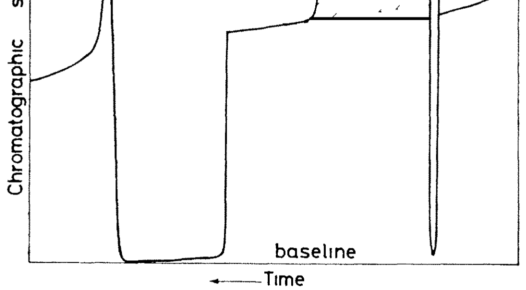

Figure 2. A reversed flow chromatogram obtained with a 6 mm internal diameter glass column of length $l' = 3$ and $l = 108$ cm, filled with 80—100 mesh 13X molecular sieve. The carrier gas was nitrogen at a flow rate 0·43 cm³ s⁻¹, the column temperature 482·6 K, and the injected reactant 2 mm³ isopropylbenzene, giving ethene as the main product.

flowing in direction R (reverse), which we term R-peaks, and another series of peaks with the gas flowing in direction F, which we call F-peaks

The analytical mathematical expressions describing the two series of elution curves (R- and F-curves) as functions of time depend on the mechanistic reaction scheme and the chromatographic characteristics of the reactant and of the product(s) The simplest case is represented by equation (1), where the reactant A is rapidly adsorbed on the active

$$\mathrm{A} + \mathrm{S} \underset{K_\mathrm{A}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{A{-}S} \xrightarrow{k} \mathrm{B{-}S} \underset{K_\mathrm{B}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{B} + \mathrm{S} \qquad (1)$$

centres S, and then is decomposed to the adsorbed product B–S, which rapidly equilibrates with the gaseous product B K_A and K_B are partition coefficients and k is a first-order rate constant for the surface reaction If $K_\mathrm{A} \gg K_\mathrm{B}$, the system of differential equations describing mass balances and rates of change, together with the appropriate initial and boundary conditions, and adsorption isotherms (assumed linear) lead, with certain approximations, to the following solution for the R-elution curve [equation (2)] Here

$$c = \frac{m}{V} kge^{-kt_{\mathrm{tot}}}[e^{k(t - t'_\mathrm{R})}]\{u(t' - t'_\mathrm{R}) - u[t' - (t'_\mathrm{R} + t_\mathrm{R})]\} + e^{-k(t - t'_\mathrm{R})}u(t' - t'_\mathrm{R}] \qquad (2)$$

c is the gaseous concentration of B which is proportional to the chromatographic signal, m the mass of A injected and g its fraction on the surface, V the volume flow rate of carrier gas, t_{tot} the total time passed from the injection of A to the last reversal of gas flow, t' the time *from* the last reversal, and u the Heaviside unit step function The F-elution curve is given by the same expression with t_R substituted for t'_R

Equation (2) predicts a square-like function for c starting at $t' = t'_\mathrm{R}$ and ending at $t' = t'_\mathrm{R} + t_\mathrm{R}$, when it abruptly becomes an exponentially decaying curve If the latter is taken as baseline, the area under the square peak (shown shaded in Figure 2) is $f = mge^{-kt_{\mathrm{tot}}}\,(e^{kt_\mathrm{R}} - 1)$, and thus a plot of $\ln f$ *vs* t_{tot} gives k from the slope Since f is proportional to t_R (or t'_R for the F-peaks), a short column length l or l' produces small narrow peaks such as 2 in Figure 2

The method has been applied to the cracking of cumene, the dehydration of propan-1-ol, and the deamination of 1-aminopropane over 13X molecular sieve The plots of $\ln f$ *vs* t_{tot} were linear, the same k was found from the R- and F-peaks, and some activation energies calculated agree with those found in the literature

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