# Choosing Catalysts for Selective Behaviour

A GRAPHICAL METHOD OF STUDYING REACTIONS

Many of the catalysts that are widely used today are capable of effecting, in addition to the reaction leading to the desired products, side reactions, or subsequent reactions of the desired products, leading to undesired products. The normal procedure for determining the conditions under which the most selective formation of desired products results is a tedious matter, involving the variation in turn of each of the relevant variables. Three recent papers (1, 2, 3) from the laboratory of Professor H. I. Waterman at the Technological University of Delft discuss the theoretical basis and application of a method designed to reduce to a bare minimum the experimentation necessary to gain this information.

Selective Reaction Schemes

There are three possible forms of simultaneous first order reactions.

(i) Consecutive reactions

$$A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } C$$
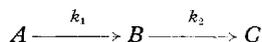
For processes of this type the following theoretical expression can be derived:

$$\alpha_B \cdot \frac{S}{S-1}(1-\alpha_A)\left[(1-\alpha_A)^{\frac{1-S}{S}} - 1\right]$$

where α_A = fraction of A reacted

α_B = fraction of initial A converted to B

$S = k_1/k_2$, the selectivity factor

When α_B is plotted against α_C (the fraction of initial A converted to C), the points lie on a curve whose position depends on S. Fig. 1 shows the curves for $S=1$ and $S=10$. We may assume that in this scheme B is the desired product and C undesired; we are therefore interested in obtaining a high

selectivity. In Fig. 1, points near X will have moderate selectivity but yields of both products will be low. At Y, the selectivity is high and the yield of B is high; at Z, the selectivity is low and the yield of B is low. The high
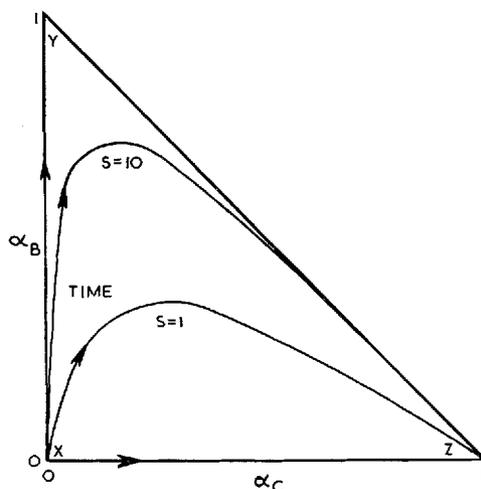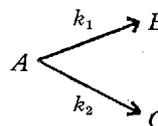

Fig. 1 Relations between α_B and α_C at various selectivities (scheme (i))

temperature (180°C) hydrogenation of linoleic ester obeys this simple scheme, the efficient selective formation of oleic ester resulting when 2 per cent nickel-kieselguhr is used at 1 atm. pressure.

(ii) Simultaneous side reactions

$$A \overset{k_1}{\underset{k_2}{\diagup\diagdown}} \begin{matrix} B \\ C \end{matrix}$$

Here again we may assume B is the desired product and C undesired. The theoretical expression is

$$\alpha_B = S\alpha_C$$

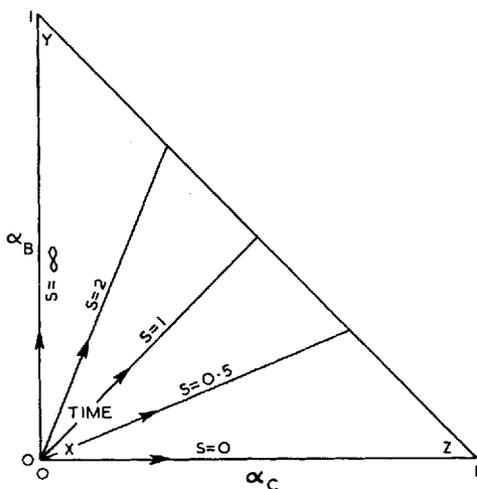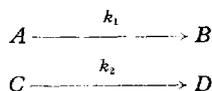where the symbols have their former mean-

Fig. 2 Relations between α_B and α_C at various selectivities (scheme (ii))

ing. The relation between α_B and α_C at various values of S is shown in Fig. 2; the points X, Y and Z also have their former significance.

(iii) Simultaneous reaction of two reactants

$$A \xrightarrow{\quad k_1 \quad} B$$

$$C \xrightarrow{\quad k_2 \quad} D$$

Here we may assume $A \longrightarrow B$ is the desired process and $C \longrightarrow D$ the undesired.
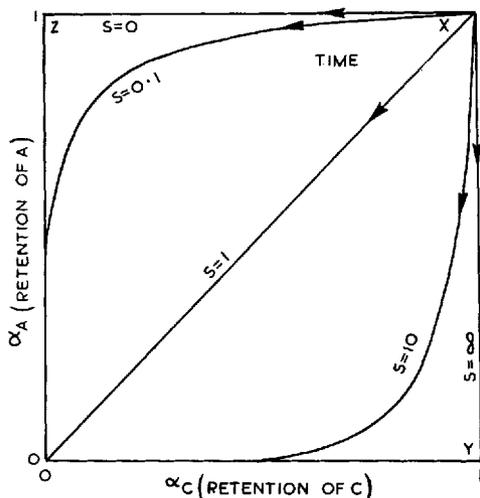

Fig. 3 Relations between α_A and α_C at various selectivities (scheme (iii))

The theoretical expression is

$$\alpha_A = 1 - (1 - \alpha_C)^S$$

where now α_A and α_C respectively mean the fractions of A and C reacted. The relation between α_A and α_C at various values of S is shown in Fig. 3, in which X, Y and Z have their usual significance.

A Generalised Treatment

Although as already noted the high temperature hydrogenation of linoleic ester conforms to one of the simple schemes, the reaction at low temperatures (20 to 90°C) does not so conform, due to interference by diffusion phenomena. Thus even in relatively simple cases the above kinetic functions inadequately predict reaction courses. In many practical cases there may be other complicating factors. In scheme (ii), for example, other products besides B and C may be formed; in scheme (iii) there may be more than two reactants; reactions may not be of the first order. Sound and yet tractable kinetic functions are impossible to derive if the system is more complex than those considered above.

A useful empirical device is described to handle the general complex case. The system is regarded as a pseudo-ternary one, in which the components are the fraction of unchanged reactant, the fraction of desired product, ij, and the fraction of by-products, x. These are related empirically by the expression

$$ij = \frac{x(1-x)}{a + bx}$$

which is the equation of a hyperbola; a and b are constants. This is the modified form of scheme (i) above. The analogous expression for scheme (iii) is

$$ij = x + \frac{x(1-x)}{a + bx}$$

Here the three components are the reactant A, the reactant C, and the combined products.

The modification of scheme (i) adequately describes the course of reaction (variation of concentrations with time) in the following systems: hydrogenation of natural oils; chlorination of hydrocarbons; the hydro-

isomerisation of hydrocarbons; and the isomerisation of methyl oleate. The modification of scheme (ii) satisfactorily describes the hydrotreating of shale gasolines.

The second paper describes in detail the application of the modified scheme (i) to the hydro-isomerisation of paraffin wax. The process resembles catalytic reforming, in that the long hydrocarbon molecules are treated with hydrogen in the presence of a catalyst, becoming highly branched: the desired products are then low pour point lubricating oils. Some undesired cracking to products boiling below 300°C also occurs. Thus the wax (A) leads to the desired product (B=oil) and to the undesired product (C=cracked products).

Using various types of platinum-alumina catalysts, the effect of several variables on the concentrations can be described by the same hyperbolic curve of Fig. 4. The maximum oil yield attainable is about 68 per cent, with about 20 per cent cracked products (point X); the conversion is therefore about 88 per cent and S is about 3.5. A higher selectivity can be obtained by sacrificing the total yield; thus at point Y, the oil yield is 50 per cent, the cracked products yield is only 5 per cent (the conversion is therefore 55 per cent), and S is 10. The effect of operating variables for a
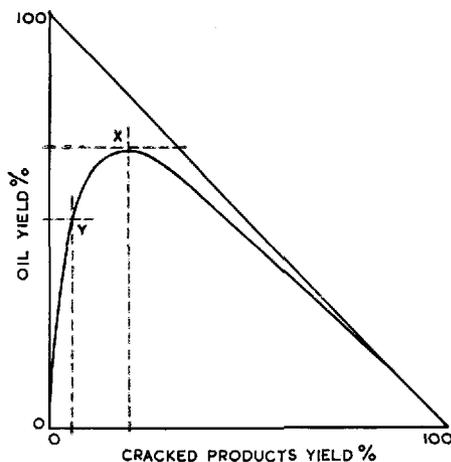

Fig. 4 *Relation between oil yield and cracked products yield for platinum catalysts in paraffin wax isomerisation*

given catalyst is shown in the second paper; the highest oil yield occurs at 425°C and with a H_2/wax molar ratio of about 50. The selectivity increases with the age of the catalyst and with its platinum and chlorine content. Replacing chloride by fluorine produces an entirely non-selective catalyst.

Screening Catalysts for Selective Behaviour

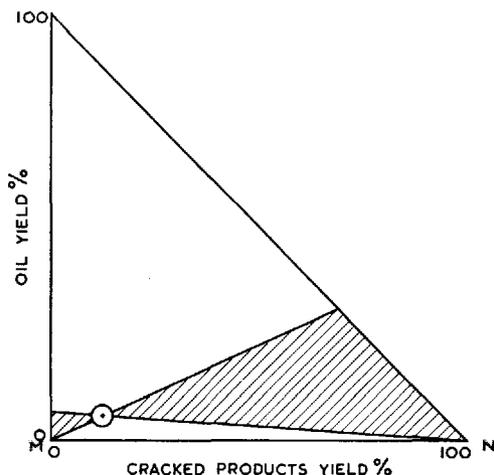The advantage of considering chemical reactions capable of showing selectivity as

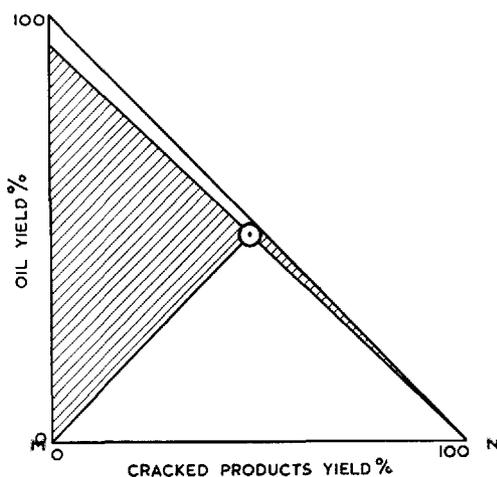Fig. 5 *Screening diagram for Al_2O_3 in paraffin wax isomerisation*

Fig. 6 *Screening diagram for $Pt-Al_2O_3-Cl$ in paraffin wax isomerisation*

pseudo-ternary systems now becomes apparent. The merit or demerit of any catalyst can largely be determined from the result of only one experiment performed under standard conditions. Consider the extreme cases shown in Figs. 5 and 6: through the one experimental point, lines are drawn through the points M and N. All the possible hyperbolas which could result from variation of any one of the operating conditions must lie within the shaded areas. Thus in Fig. 5, where the catalyst is Al_2O_3 alone, the maximum possible oil yield at 100 per cent conversion is about 30 per cent and S is about $\frac{1}{2}$, whereas at the other extreme in Fig. 6 (where the catalyst is platinum on alumina containing chlorine) the maximum oil yield at 100 per cent conversion is greater than 90 per cent and S is infinity. The standard operating conditions are: 435°C, 51 atm., WHSV =0.97 and a H_2/wax molar ratio of 94. Therefore on the basis of only one experiment it is confidently predicted that variation of any of these conditions will never result in a highly selective performance by Al_2O_3 alone, whereas, for example, lowering the temperature with the $Pt-Al_2O_3-Cl$ catalyst may cause it to show a high selectivity.

On the basis of the results shown in the second paper the order of expected selectivity for various catalysts is $Pt-Al_2O_3-Cl > MoO_3-Al_2O_3-F = CoMoO_4-Al_2O_3 > Pt-SiO_2-Cl > Al_2O_3-Cl = Al_2O_3$. The authors believe the method can be developed into a more general, efficient means of screening catalysts and evaluating reactions in which selectivity is involved.

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References

1 H. I. Waterman and A. B. R. Weber . .   *J. Inst. Petroleum*, 1957, **43**, 315–322

2 H. Breimer, H. I. Waterman and   *Ibid.*, 299–306
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3 H. I. Waterman, C. Boelhouwer and   *Anal. Chim. Acta*, 1958, **18**, (5), 497–507
   J. Cornelissen

Platinum-coated Titanium Anodes

POSSIBILITIES IN INDUSTRIAL ELECTROLYSIS

The important discovery that a thin layer of platinum applied to the surface of titanium provides an economic non-consumable electrode was reported by J. B. Cotton of ICI Metals Division in *Platinum Metals Review* in April. The titanium acts as a bulk carrier of current, while the platinum provides an escape path for the current to enter the solution; small corrosion currents are quickly stifled as polarisation ensues. The platinum coating need not be impervious or continuous, and the electrodes will carry high anodic current densities in many types of solutions.

Commenting further on this development in the June issue of *The Industrial Chemist*, R. J. Watkins, also of ICI Metals Division, draws attention to the advantages of platinum-faced titanium anodes by comparison with carbon anodes in terms of much higher current density limits in many types of electrolytes and of the lightness and better mechanical properties of titanium.

Trials are already taking place with these new anodes for cathodic protection of ships and other marine structures by impressed current techniques, but a further most promising development lies in their use in industrial electrolytic cells for the manufacture of chemicals. In addition investigations are in hand on the possibility of employing them for electro plating, electro-descaling and electro-reduction.