Yield Enhancement in a Chromatographic Catalytic Reactor

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Summary A careful study of the catalytic dehydrogenation of cyclohexane to benzene ($C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$) in a gas chromatographic reactor has provided direct evidence for the displacement of an equilibrium and an enhancement in product yields in such reactors.

The yields of useful products from conventional flow reactors are ultimately limited either by the value of the equilibrium constant or by the consumption of a primary product by secondary reactions. By combining in one reactor both catalytic and chromatographic functions and by using pulse techniques, both these limitations can be removed. The back reaction can be minimised by chromatographically separating the products from each other while secondary reactions can be reduced by retaining the primary product on the column relative to the reactant pulse. Although there have been several experimental and theoretical studies of equilibrium displacement in small bore columns,[1-4] the evidence for displacement is equivocal. A comparison is made between experimental yields and estimated equilibrium yields which involves many assumptions, and in addition there are unusual and unexplained features in some of the experiments reported (*e.g.* the effect of the ratio of pulse size to column length on conversion)[2]. Here we report the results of a careful study of the dehydrogenation of cyclohexane to benzene and hydrogen in a chromatographic reactor which we believe provide more direct evidence for displacement and which are in accord with the theoretical predictions of Gore[4] who used digital methods to treat the effects of finite equilibration rates on the extent of displacement.

The catalyst used was 0 72% w/w platinum on Woelm chromatographic silica prepared by the 'amine complex' method of Dorling and Moss[5] and reduced at 300 °C under hydrogen The Brunauer–Emmett–Teller surface area was 525 m^2 g^{-1} while that of the platinum was 0 25 m^2 g^{-1} corresponding to a crystallite size of 15 Å The reactor consisted of two sections, both of 4 mm diameter, the catalyst section containing the platinum on silica whose length was varied from 0 06 to 1 m was followed by an analytic section of 0·30 m length carrying only Woelm silica where the components were further separated before detection by a Taylor Servomex microkatharometer (Type GC 197) and measurement by a Hewlett Packard 3373B integrator The temperatures of the two sections could be varied independently, that of the reactor requiring very precise control which was achieved to ± 0 5 °C by using an air thermostat linked to a Mini-Therm proportional controller as a temperature trimmer Helium was used as carrier gas after removal of impurities by passage through a 1 m tube length of silica (rapid catalyst deactivation occurred if the helium was not carefully purified)

The Figure shows the effect of flow rate and hence residence time [proportional to (flow rate)$^{-1}$] on the degree of conversion, α, of cyclohexane into benzene and hydrogen for a 1 μl pulse injected into a 0 06 m reactor at various temperatures The measured values of α are those resulting from numerous repeated experiments under the same conditions and show a standard deviation of less than 2% Also shown are the equilibrium values of α calculated by graphical and numerical methods using the measured pressure in the reactor and the width of the cyclohexane peak to determine the ratio of helium to cyclohexane in the reacting pulse Similar effects are observed with other pulse sizes and bed lengths The unusual and interesting feature is the rise in the experimental α values to well above the equilibrium values as the flow rate is increased from 0 14 to 0 67 cm^3 s^{-1} before they fall below the equilibrium values at the higher flow rates No such maximisation in α with changing flow rate can occur if equilibrium obtains but this is readily explicable if displacement occurs At very low flow rates the residence time is long enough for equilibrium to be attained but the flow is too low for effective displacement of the hydrogen away from the benzene and hence, as found, the α values are fairly close to the equilibrium values with a small increase in α with decreasing flow At very fast flow rates the rate of the catalysed reaction is too slow for even the equilibrium state to be achieved and the experimental α values fall well below the equilibrium values Between these two extremes we have the optimum conditions for displacement, the residence time is long enough for the system not to be limited kinetically but the flow rate is still rapid enough to ensure appreciable separation of the hydrogen and benzene so that the conversion can rise well above the equilibrium level We believe, therefore, that the observation of such a maximisation in conversion with flow rate (which does not rely on calculated values of conversion) constitutes very strong evidence for the occurrence of displacement and points to its potential application in commercial processes Such a maximum for a chromatographic reactor has been predicted by Gore[4] but unfortunately his use of a first order rate law makes a direct comparison difficult since the dehydrogenation of cyclohexane will probably show a zero order dependence on the cyclohexane concentration[6]

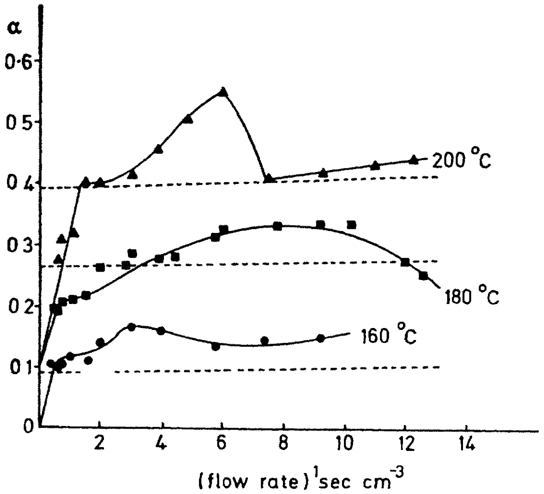

FIGURE The effect of (flow rate)$^{-1}$ on conversion The dashed lines indicate calculated values of the degree of conversion α based on an undisturbed equilibrium (The 180 and 200 °C curves have been displaced upwards by 0 1 units of α for clarity)

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