Experimental Technique for Kinetic Study of Hydrogenation of Fatty Acid Methyl Esters in Vapor Phase

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ABSTRACT

A new approach to kinetic studies of fat hydrogenation is discussed. An experimental setup is described in detail. An example of reactor performance in hydrogenation of fatty acid methyl esters is given.

INTRODUCTION

Kinetic studies in fat hydrogenation are generally performed in scaled-down models of reactors which are in common industrial use. The only exception is the work by Mounts et al. (1-3) in which a vapor-phase microreactor was used.

To simplify the reaction system in our studies, methyl esters of fatty acids have been used as model substances. In addition to nickel catalysts, other catalysts such as copper, platinum, and palladium have been investigated. In this work, which aims to clarify special catalytic properties of different metals, it is desirable to perform a study of the surface processes alone. If mass transfer limitations are present, the selectivity of consecutive and parallel reactions may be altered and it may not be possible to identify the intrinsic properties of the catalyst.

A new approach to kinetic studies of fat hydrogenation is described in this first paper.

ON THE CHOICE OF METHODS

Liquid-Phase vs. Gas-Phase Experiments

The state of the art in catalytic research would be drastically improved if reaction intermediates could be analyzed in detail on the catalyst surface during the course of the reaction. This is feasible, however, only for very simple systems at ultrahigh vacuum. The design effort must therefore be directed towards the construction of experimental equipment in which temperature and concentration gradients are minimized. If no transport limitations exist, standard analytical equipment will yield direct information on the conditions close to the catalytically active surface in the pores of the catalyst support.

With slurry reactors, as in fat hydrogenation, we find that elimination of transport limitations may be difficult. The limitations of external concentration gradients and pore diffusion in laboratory work on fat hydrogenation has been reported by several authors (4-7).

The external mass transfer resistances may be decreased by increasing the stirrer rate, but it is generally not possible to eliminate the influence of hydrogen transfer. Concentration gradients of fatty acids are of less importance.

Pore diffusion rates may not be increased by vigorous stirring. Calculations by Bern et al. (4) reveal that reaction rates are generally affected by hydrogen pore diffusion limitations in kinetic studies of fat hydrogenation.

Elimination of pore transfer resistances may be achieved with a less active catalyst, i.e., by lowering the reaction rate rather than increasing diffusion rates. This is not a successful approach in a slurry reactor, however, since the maximum possible catalyst load per unit volume of reactant is too small. A substantial decrease in catalytic activity would not yield a sufficiently high reaction rate. The rate of change of reactant and product concentrations would be too small and would lie within the errors of the analytical method.

The difficulties met in slurry reactor experiments may, in general, be overcome in gas-phase solid catalyzed systems. Experimental methods for gas-phase systems are better developed, partly due to the large research effort in the petrochemical field. The apparatus may easily be equipped for continuous and nonstationary experiments. A large number of laboratory reactors for kinetic studies of heterogeneously catalyzed reactions has been described in the literature. Excellent reviews have been published by Weekman (8), Sunderland (9), and Smith (10).

In gas-phase laboratory reactors, the number of moles of reactant per gram catalyst is generally less than 10^{-3}. For slurry reactors the corresponding quotient approaches 1 mol/g catalyst. Thus, the catalysts used in gas-phase reactors may be one thousand times less active than those used in slurry reactors and yet conversion may be maintained.

Dynamic vs. Steady-State Methods

Bennett (11) and Kobayashi et al. (12) point out that dynamic methods, if properly applied, yield more information than steady state methods on mechanisms of heterogeneously catalyzed reactions. At steady state, all reaction steps, mass transfer steps as well as chemical steps, proceed at equal rates. If no mass transfer limitations are present, the reaction scheme still contains a sequence of steps, such as adsorption, surface reaction and desorption, which are not readily identified and separated on the basis of steady state data.

Kobayashi et al. (12) discussed the additional information which can be extracted from step response experiments. Theoretical analysis reveals that the response curve resulting

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Notation: c, outlet concentration, mol/m^3; c_o, inlet concentration, mol/m^3; c_b, concentration in bulk fluid, mol/m^3; c_s concentration at catalyst surface, mol/m^3; d, pore diameter, m; D_e, effective diffusivity, m^2/s; E, activation energy of reaction, J/mol; h, heat transfer coefficient, J/m^2 s K; ΔH, heat of reaction, J/mol; k_c, mass transfer coefficient, m/s; p, partial pressure, Pa; p_o, saturated vapor pressure, Pa; q_f, total flow to reactor, m^3/s; q_{rec}, recycle flow, m^3/s; R, observed reaction rate per unit particle volume, mol/s m^3; R_g, gas constant, J/mol K; r, observed reaction rate per unit mass of catalyst, mol/kg s; r_p particle radius, m; T_b, temperature of gas in bulk flow, K; T_s, temperature of gas at catalyst surface, K; $\bar{v}$, molar volume, m^3/mol; V, volume of catalyst bed, m^3; W, catalyst mass, kg. Greek symbols: σ, surface tension, N/m; λ_e, effective thermal conductivity of catalyst particle, J/m s K.

from a step change in the concentration of one reactant yields information about the amount adsorbed on the surface and rates of adsorption and desorption.

Batch vs. Continuous Operation

The theoretical part of a kinetic study involves postulation of physically sound reaction mechanisms and estimation of several parameters, e.g., rate and equilibrium constants, in the rate laws derived from the postulated mechanisms. Evaluation is facilitated if reaction rates can be calculated from experimental data in a simple and accurate way. In a perfectly mixed reactor with continuous flow, the rates can be determined directly from inlet and outlet concentrations. A batch or semibatch reactor, e.g., a slurry reactor, is more complex and gives less accurate data, since reaction rates must be calculated from time derivatives of reactant and product concentrations.

Conclusions

Thus, an efficient tool to elucidate reaction mechanisms in hydrogenation of fatty acid methyl esters may be a reactor with perfect mixing with continuous flow. It should be designed for steady state and dynamic experiments in the gaseous phase.

Reactant concentrations are substantially lower in the gas phase than in the liquid phase, and the results in gas-phase reactors must be subject to critical examination and be compared to slurry reactor data.

APPARATUS

The major components of the apparatus are reactant feed subsystem, reactor and analytical devices. The apparatus is intended for studies of gas-phase/solid catalyzed reactions. One of the reactants may be a liquid at room temperature and atmospheric pressure, since the reactant feed system is furnished with evaporators. The design permits steady state experiments and step response experiments. A schematic flow diagram of the apparatus is shown in Figure 1.

Reactant Feed

For ease of experimentation in steady state runs and to facilitate step response experiments, the system has been furnished with two parallel feed lines. Flow and concentrations may be set independently in the two feed lines.

Inert gas is fed via a flow meter and flow controller to a mixing point, where hydrogen is added via the same facilities. Both gas flows may be measured separately. The system also has a meter for total gas flow measurements.

Vaporization of methyl esters into a gas system is not readily done in small-scale equipment. Spray nozzles for extremely low flow rates are very difficult to fabricate since satisfactory atomization requires a high pressure drop and consequently extremely fine holes. Unless atomization is good, methyl ester concentrations will exhibit severe oscillations. A simpler way to achieve stable and controlled vaporization of the methyl esters has been sketched in Figure 2.

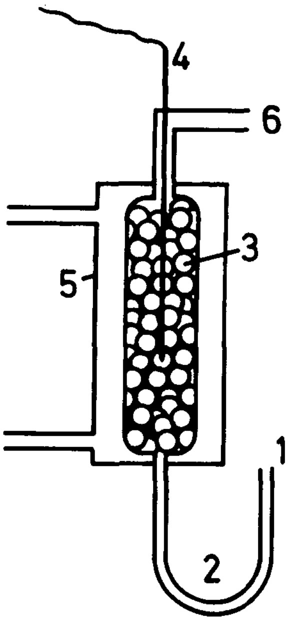

FIG. 2. Evaporator. (1) Gas inlet; (2) U-tube; (3) glass bed; (4) thermocouple; (5) jacket; (6) gas outlet.

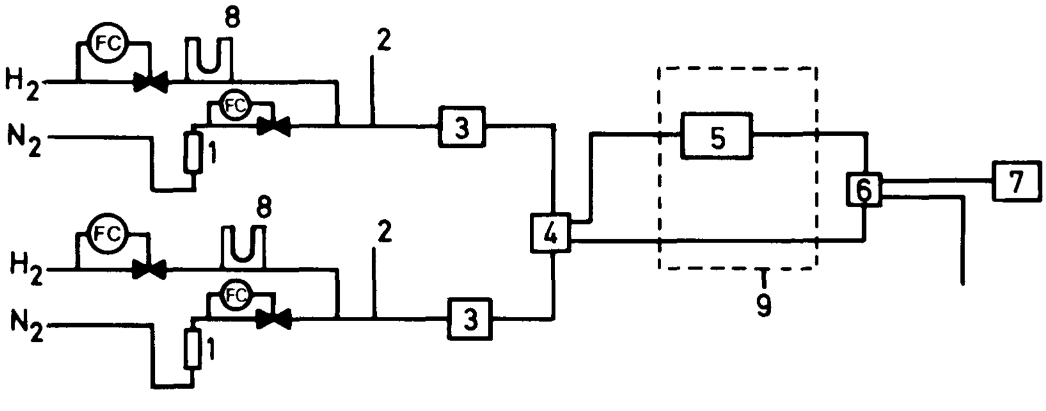

FIG. 1. Schematic flow diagram of the apparatus. (1) Flow meter, inert gas; (2) flow meter, total flow; (3) evaporator; (4) switch; (5) reactor; (6) switch; (7) GC; (8) flow meter, H_2; (9) oven.

From the U-tube at the inlet side of the evaporator, liquid methyl ester is transferred into the glass sphere bed by the hydrogen/nitrogen mixture. The temperature of the glass bed is controlled by a constant temperature bath. The gas leaving the bed is saturated with methyl ester, so that the partial pressure of ester in the exit gas is set by the bed temperature.

Reactor

In the discussion above, the following demands were placed on a reactor for kinetic work: negligible temperature and concentration gradients, a high ratio of catalyst to reactants, and perfect mixing in the bulk. A perfectly mixed reactor with continuous flow may be designed to posess nearly all desirable qualities.

Perfectly mixed reactors for gas-phase/solid catalyzed reactions are generally fixed bed reactors with recycle. The highest ratio of catalyst to reactants will be obtained in internally recycled reactors. There are several reactors of this kind described in the literature (8-10). Our choice fell upon Sunderland's and El Kanzi's (13) "vibration mixed reactor," which was slightly modified. Details of the reactor are shown in Figure 3.

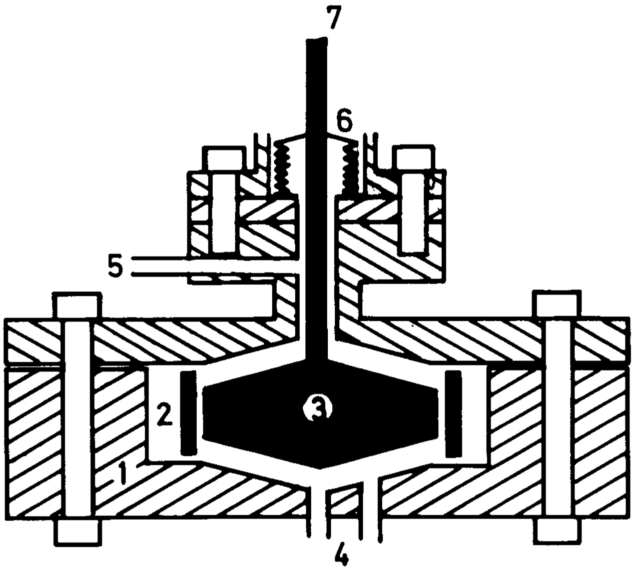

FIG. 3. Reactor. (1) Main body; (2) catalyst space; (3) piston; (4) outlets; (5) inlet; (6) sealing bellow; (7) piston rod.

Mixing of the gas was done by a piston reciprocating at 20 cycles/sec. The piston was connected to a motor via a rod excentrically mounted on the motor axis. A metal bellow sealed the rod. There were 20 holes drilled into the main body of the reactor around its perimeter, each hole large enough to take four catalyst particles on top of each other. A thermocouple inserted in a hole in the reactor body close to the catalyst allowed the temperature to be measured.

External mass and heat transfer characteristics were estimated by Sunderland and El Kanzi (13) using the method of Yang and Hougen (15,16). They compared their predictions to results from test runs in which *o*-xylene was oxidized over a vanadium pentoxide catalyst. Their conclusion was that mass and temperature gradients were small even under severe conditions. They also concluded that the method of Yang and Hougen is appropriate, although the direction of the gas flow changes in their reactor.

Since our reactor is not an exact copy of Sunderland's and El Kanzi's and since it is intended for hydrogenation of fatty acid methyl esters, the characteristics of the reactor have to be explored once more.

Macromixing was examined by the step response method. The residence time distribution, calculated from the response to a step change of nonreacting gas concentration in the feed, agrees well with that of a perfectly mixed reactor with continuous flow. Interparticle and intraparticle gradients of concentrations and temperature must be examined in each experiment. An example of reactor calculations including mass and heat transfer limitations is given in the last paragraph of this paper.

Analysis

The exit gas from the reactor was analyzed by an on-line gas chromatograph. A switching valve made possible the analysis of the flow from the evaporator not connected to the reactor.

HYDROGENATION OF METHYL LINOLEATE

An example of the reactor performance in a kinetic study is given below.

Mass and Heat Transfer

To ensure that the data obtained reflect only chemical events, gradients must be eliminated within the particles and the film surrounding them. The following criteria are commonly used to examine the existence of transport limitations. They have been reviewed by Mears (14).

Mass transfer resistance in the pores of a spherical isothermal particle with first-order reaction may be neglected if

$$\frac{R\, r_p^2}{c_s D_e} < 1 \qquad [1]$$

All symbols are given at the beginning of the paper.

The lack of intraparticle temperature gradients is established by applying

$$\frac{|\Delta H|\, R\, r_p^2}{\lambda_e\, T_s} < \frac{T_s\, R_g}{E} \qquad [2]$$

The temperature between the external catalyst surface and the bulk fluid is negligible if

$$\left| \frac{-\Delta H\, R\, r_p}{h\, T_b} \right| < 0.15\, \frac{R_g\, T_b}{E} \qquad [3]$$

Finally, for first-order reactions, the concentration gradient between bulk fluid and catalyst surface is less than 5% if the following is valid:

$$\frac{R\, r_p}{c_b\, k_c} < 0.15 \qquad [4]$$

The mass and heat transfer coefficients k_c and h may be estimated from the j-factor equations given by Yang and

Hougen (15,16). The four criteria described above yield maximum allowable reaction rates for negligible transport resistances. The reaction rates determined from experiments must be well below the lowest of these maxima.

Macromixing

For ease of calculation, the macromixing characteristics of the internally recycled reactor used here should be similar to that of completely mixed reactor with continuous flow. This can be tested by applying the criterion given by Luft (17).

$$q_{rec}/q_f < 50 \qquad [5]$$

and the more sophisticated criterion by Nyström (18) which gives the minimum recycle flow for complete mixing in the bulk flow and negligible pore transport resistance. The minimum recycle flow is given by

$$q_{rec} > 10 \frac{D_e V}{r_p^2} \qquad [6]$$

Condensation in Catalyst Pores

Since the boiling point of methyl esters is very high (above 400 C), there exists a maximum partial pressure for each reaction temperature. At partial pressures above this limiting value, condensation occurs. In the narrow pores of the catalyst this takes place at partial pressures below the vapor pressure in the bulk. The critical point can be determined from the Kelvin equation for capillary condensation

$$\ln \frac{p_o}{p} = \frac{4\sigma \bar{v}}{d R_g T} \qquad [7]$$

Results

Based on the preceding calculations, the experiments may be approved or rejected once the reaction rate has been determined from experimental data. This is straightforward since the reactor is perfectly mixed. The rate is given by a simple mass balance

$$r = \frac{q_f}{W} (c_o - c) \qquad [8]$$

The results of one calculation are given in Table I.

The calculations presented in Table I reveal that pore diffusion is the limiting transport process. Thus the maximum allowable reaction rate is 6 × 10^{-6} mol/kg catalyst. The observed reaction rates, given in Table II, are below this limiting value. The conclusion may then be drawn that no transport limitations are operating. Similar comparisons may be carried out for condensation and macromixing effects.

This run is part of an experimental material which will be published in the near future.

TABLE I

Limiting Values Calculated from Various Criteria

Type of limiting step	Limiting magnitude	Limiting value	Criterion
Internal mass transport	Maximum reaction rate	6 × 10^{-6} mol/s kg cat	Eq. 1
Internal heat transport	Maximum reaction rate	0.59 mol/s kg cat	Eq. 2
External heat transport	Maximum reaction rate	0.01 mol/s kg cat	Eq. 3
External mass transport	Maximum reaction rate	0.1 mol/s kg cat	Eq. 4
Complete bulk mixing	Minimum recycle flow	42 mL/s	Eq. 5
Complete bulk mixing and negligible internal transport resistance	Minimum recycle flow	120 mL/s	Eq. 6
Capillary condensation	Maximum partial pressure	3 × 10^{-3} bar[a]	Eq. 7

[a] 1 bar = 0.987 atm.

TABLE II

Experimental Conditions

Total pressure		1.02 bar
Feed composition:	methyl oleate	5.3 × 10^{-3}%
	methyl linoleate	2.9 × 10^{-2}%
	hydrogen	3.2%
	nitrogen	96.8%
Exit composition:	methyl stearate	7.5 × 10^{-3}%
	methyl oleate	2.3 × 10^{-2}%
	methyl linoleate	4.1 × 10^{-3}%
Flow rates:	feed	0.87 mL/s
	recycle	200 mL/s
Temperature		180 C
Rate of methyl linoleate consumption:		3.66 × 10^{-6} mol/s kg cat
Rate of methyl stearate formation:		1.09 × 10^{-6} mol/s kg cat

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