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A TUBULAR MICRO-REACTOR FOR MEASUREMENT OF THE KINETICS OF LIQUID PHASE HETEROGENEOUS REACTIONS UNDER PRESSURE

By

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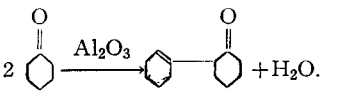
Abstract

A plug-flow tubular micro-reactor for kinetic studies of heterogeneous reactions in liquid phase under elevated pressure is designed. The reactor is packed with fine particles of catalyst (30~60 μm). The possibility of diminishing interphase transport, intraparticle diffusion and axial dispersion effects is discussed. The alumina catalysed aldol condensation of cyclohexanone at 250°C and 10 atm was used as a test reaction.

Introduction

Although a tubular flow reactor is rarely used for kinetic measurements of heterogeneous liquid phase catalytic reactions, it appeared as the best experimental arrangement for kinetic study of aldol condensations.[1] The evaluation of kinetic experiments from a tubular flow reactor is possible if the reaction is influenced by interphase transport intraparticle diffusion and axial dispersion only negligibly.[2~5] The purpose of this work is to design a micro-reactor which satisfactorily approximates an ideal isothermal plug-flow tubular reactor (PFTR). The alumina catalyzed aldol condensation of cyclohexanone was chosen as a test reaction,



Before designing a laboratory reactor kinetic measurements of liquid-phase heterogeneous reactions one has to keep in mind the physical properties of liquid phase and conditions of such kinetic measurements. The main differences between the gas- and liquid-phase measurements are listed in Table 1.

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TABLE 1. The important differences between properties of gas and liquid phases and between conditions for gas- and liquid-phase kinetic measurements

Properties and Conditions	Liquid Phase	Gas Phase
Density, ρ [g/cm^3]	0.5~1.5	1×10^{-3}~5×10^{-3}
Viscosity, μ [cP]	0.2~2	1×10^{-2}~3×10^{-2}
Diffusion coefficient, $\mathscr{D}$ [cm^2/s]	2×10^{-5}~1×10^{-4}	0.1~0.5
Interstitial flow velocity, u [cm/s]	0.002~0.2	1~100
Reynolds number, Re[a)]	1×10^{-6}~1×10^{-3}	1×10^{-2}~10
Thermal conductivity [W/m. deg]	0.1~0.15	0.01~0.05

a) Calculated for particle diameters d_p=0.1~1 mm

In liquid-phase heterogeneous reactions the effects of intraparticle diffusion and interphase transport are enhanced by slower diffusion of reactants in comparison with gas-phase reactions. Because of very low Reynolds numbers (Table 1), the interphase transport in liquid phase is influenced only slightly by the change of interstitial flow velocity.[2,3] The above mentioned effects depend, however, significantly upon the size of catalyst particles.[3] Thus, for a liquid phase reaction the interphase transport and the intraparticle diffusion can be experimentally tested only by changing the particle size. Therefore, we have to use particle sizes one or two orders of magnitude smaller than usual sizes in gas-phase measurements. On the other hand, the high thermal conductivities of liquids and the use of small catalyst particles in narrow beds restrain the possible temperature gradients.

The flow nonideality in a tubular reactor is usually described as axial dispersion and characterised[3,6] by dimensionless Bodenstein number Bo, which includes the effective dispersion coefficient E. The percent error p caused by axial dispersion in kinetics can be estimated by the relation derived by Mears[5,7]

$$p \leq \frac{100\, n d_p}{Bo\, L} \ln\left[1/(1-x)\right]. \qquad (1)$$

In contrast to intraparticle diffusion and interphase transport, the effect of axial dispersion can be hardly tested by kinetic experiments. For catalyst beds of fine particles (5~100 μm) the reproducibility of packing procedure is poor and thus dilution of catalyst by inert particles recommended for gas-phase reactions[5] is not feasible. The extent of axial dispersion must be, therefore, estimated experimentally.

The simplest method available for determination of E or Bo is the

pulse injection.[3,6] A tracer is injected into a fluid flowing through reactor and the outlet concentration of the tracer is continuously measured. However, if the bed is packed with porous catalyst particles, the time dependence of the outlet concentration of the tracer is influenced not only by axial dispersion but also by tracer adsorption and intraparticle diffusion.[8] The shape of the tracer outlet signal can be characterised[3,6] by the plate height H defined as

$$H = L\sigma_t^2/t_r^2 . \qquad (2)$$

The dependence of H on interstitial flow velocity u is expressed by the van Deemter equation.[8,9]

$$H = A + B/u + Cu . \qquad (3)$$

Because of the low diffusion coefficients in the liquid phase, the contribution of molecular diffusion to axial dispersion, which is included in B, can be neglected.[10] In Eq. (3), A includes the eddy diffusion contribution to axial dispersion, whereas C involves diffusion and adsorption effects.[8]

Thus, for liquids flowing through beds of porous particles the approximative relationship between A and Bodenstein number Bo could be expressed as

$$A \approx 2d_p/Bo . \qquad (4)$$

It has been pointed out that Bodenstein number does not depend for liquids upon Reynolds number.[11] Therefore, values of Bo estimated by pulse technique (Eqs. (2)~(4)) can be used to calculate the approximate error p from Eq. (1) although the hydrodynamic conditions of pulse measurements differ from conditions for kinetic experiments.

Experimental

Cyclohexanone (Lachema, Czechoslovakia) analytical grade, was used without further purification. Aluminium oxide (Brockman's II, Reanal, Hungary) was sieved and elutriated in water-ethanol mixture (1:1, v/v). Fractions 30~40 μm (d_p=35 μm) and 40~60 μm (d_p=50 μm) were decantated in distilled water, filtered off and dried at 400°C for 6 hours.

The apparatus (Fig. 1) consisted of a reciprocating micropump, a PFTR reactor, a calibrated glass tube used as a flow-meter and a stainless steel receiver for collecting reaction products. The receiver was maintained under constant pressure (10 atm) of nitrogen. Reaction mixture samples for analysis were withdrawn from the reactor outlet stream by means of a four-port valve. The reactor (Fig. 2) was packed with alumina catalyst by the "tap

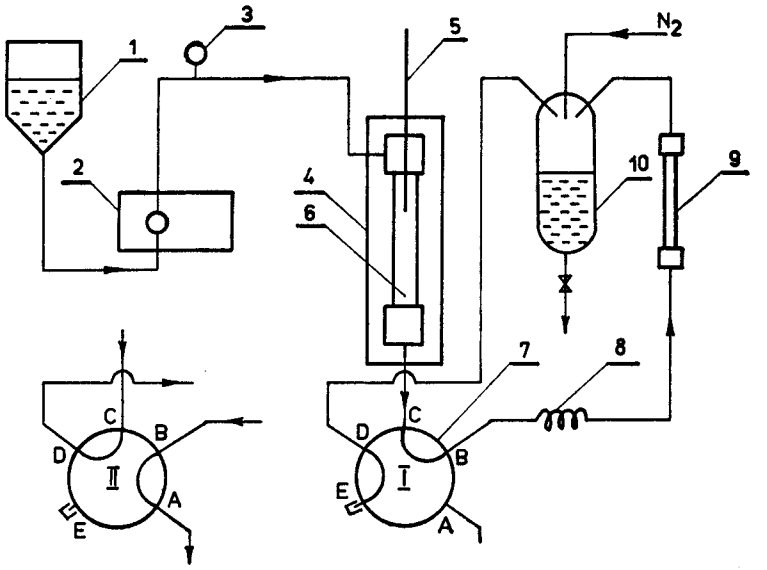

Fig. 1. Kinetic apparatus. 1) Feed reservoir, 2) Reciprocating pump, 3) Manometer, 4) Heating mantle, 5) Thermocouple, 6) Reactor, 7) Four-port valve (E-closed), 8) Capilary coil (20 cm×0.2 mm), 9) Flow-meter, 10) Reaction product receiver. Positions of four-port valve: I) Working position, II) Sampling and purging position.

and bounce" technique.[12] The upper part of the reactor was packed with glass ballotini (100 μm) and served as a feed preheater. Reactor temperature was maintained within ± 0.5°C by means of a proportional temperature controller.

The activity of catalyst reached approximately a constant value after 2 hours at 250°C. Catalyst activity was checked during the kinetic measurement by control experiments at fixed conditions (*e. g.*, $W/F = 12.1\ g_{cat}$ hr/mol). Analysis of reaction mixtures were performed by gas chromatography using 1.7 m×3 mm column packed with Silicone OV 17 (7% wt.) on Gas-Chrom Q.

When the tracer dispersion was measured, the upper reactor fitting was replaced by a septum. Solution of benzene in methanol (5% vol.) was used as the tracer and pure methanol as the flowing liquid; 0.5 $\mu\ell$ of the tracer was injected onto the upper end of the catalyst bed through the septum. The time dependence of the tracer concentration at the reactor outlet was followed by means of an UV-detector (254 nm) with 10 $\mu\ell$ flow cells.

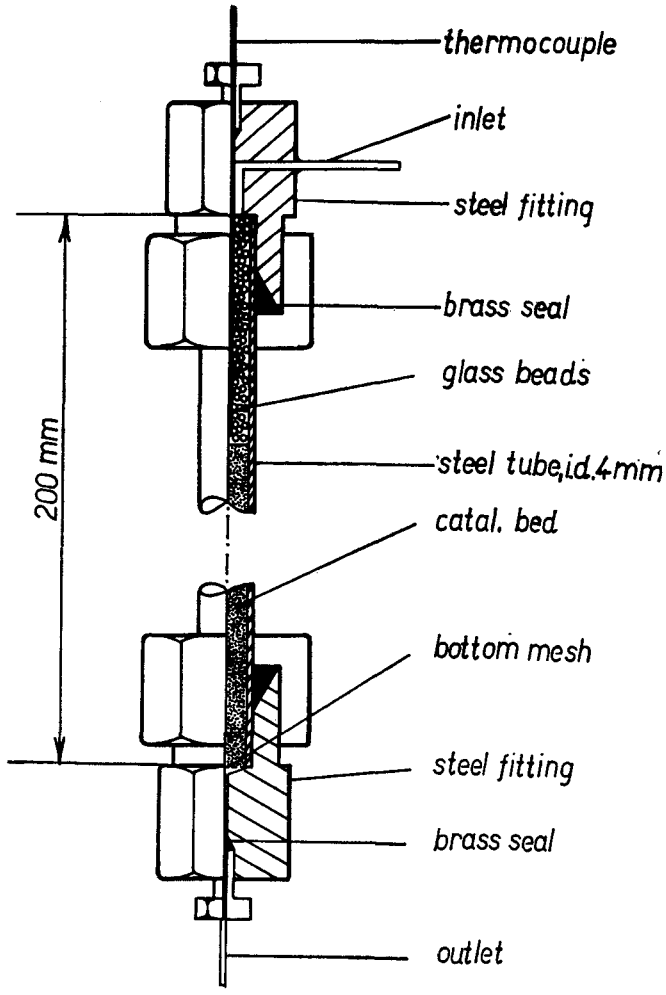

Fig. 2. A schematic diagram of PFTR (not to scale).

Results and Discussion

The linear plots of H against u obtained for both catalyst size fractions are shown in Fig. 3. The values of Bo calculated from intercepts A in Fig. 3 are 0.17 and 0.21 for $d_p=35\,\mu$m and 50 μm, resp. The experimental dependences of cyclohexanone conversion x on W/F for both catalyst fractions are given in Fig. 4. Reaction order, n, of the alumina catalysed condensation of cyclohexanone estimated by the method of fractional-life period is about 3. Using Eq. (1), errors p were estimated for the above values of

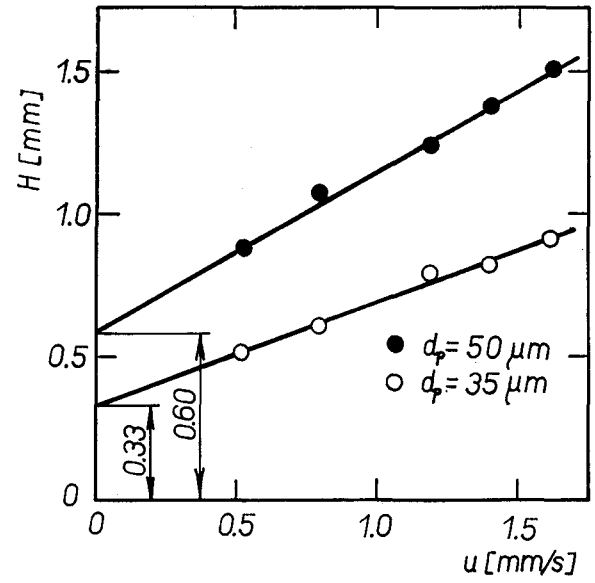

Fig. 3. Linear dependence of plate height H on linear flow velocity u obtained by pulse measurement. Flowing liquid-methanol, tracer-benzene, temp. 25°C.

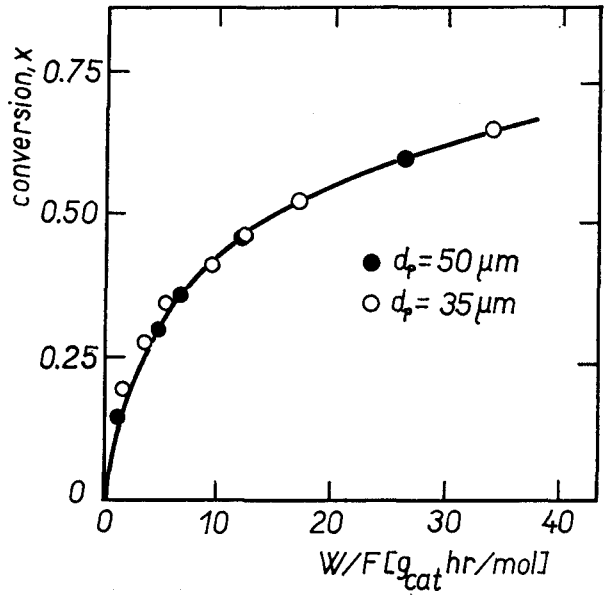

Fig. 4. Experimental dependence of cyclohexanone conversion x on W/F. Catalyst weight $W = 2.05$ g.

Bo, d_p, n and $L=150$ mm and for the highest conversion achieved ($x=0.7$). The maximum error p due to axial dispersion was 0.35% and 0.55% for $d_p=35\,\mu$m and $50\,\mu$m, respectively.

Experimental points for both catalyst size fractions fall on a single curve (Fig. 4). This is the evidence that intraparticle diffusion and interphase transport have negligible effect on conversion x. Different criteria have been proposed for testing the above effects, but in all of them several parameters must be estimated independently. We have used criteria proposed by Mears[4] for their simplicity. In Table 2, the parameters used for evaluation of criteria (5) and (6) are listed. The intraparticle diffusion is excluded, if the criterion (5) is fulfilled

$$rd_p^2/c_s D<1/|n|\,. \qquad (5)$$

TABLE 2. Parameters for criteria (5) and (6)

Parameter	Derived from	Value
Feed density, ρ, at 250°C, 10 atm	Watson generalised diagram[13]	0.69 [g/cm^3]
Diffusion coefficient, $\mathscr{D}$, of cyclohexanone, at 250°C	Wilke relationship[14]	6.5×10^{-5} [cm/s]
Concentration c_s, c_b	Inlet feed density	7×10^{-3} [mol/cm^3]
Maximum reaction rate, r	Experimental dependence, $x=x(W/F)$	7×10^{-5} [mol/g$_{cat}$ s]
Reaction order, n	"	3
Effective diffusion coefficient, D, at 250°C	$D=\varepsilon\mathscr{D}/\xi\doteq\mathscr{D}\times10^{-1}$	6.5×10^{-6} [cm/s]
Mass transfer coefficient, k_c	$k_c\doteq2\mathscr{D}/d_p$	2.5×10^{-8} [1/s]
Particle diameter, d_p	Experimental value	5×10^{-3} [cm]

An analogous criterion (6) is used for interphase transport

$$rd_p/c_b k_c<0.15/n\,. \qquad (6)$$

Both criteria are fulfilled, because

$$4\times10^{-2}<1/|n|$$

$$2\times10^{-3}<0.15/n\,.$$

Therefore, we suppose that the interparticle diffusion and interphase transport have negligible effect on kinetics in our PFTR. Estimated reaction enthalpy[15] of aldol condensation of cyclohexanone is only 3.5 kcal/mol and the reactor is assumed to be isothermal.

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NOTATION

Bo	Bodenstein number (ud_p/E)
c_b	bulk concentration of reactant
c_s	surface concentration of reactant
D	effective diffusivity of reactant in porous catalyst
$\mathscr{D}$	diffusion coefficient
d_p	diameter of catalyst particle
F	molar feed rate
k_c	mass transfer coefficient
L	length of catalyst bed
r	experimentally determined reaction rate
Re	Reynolds number ($d_p u\rho/\mu$)
u	linear interstitial velocity
W	catalyst weight
x	reactant conversion
σ_t^2	variance of tracer concentration
ε	particle porosity
ξ	tortuosity

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