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Supported Liquid-Phase Catalysis

III. Experimental Evaluation of the Diffusion-Reaction Model

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The theoretical model for transport and reaction in supported liquid-phase catalysis (SLPC) proposed in Part I (R. Datta and R. G. Rinker, *J. Catal.* 95, 181, 1985) was tested experimentally using two different homogeneously catalyzed model reactions. The hydrogenation of ethylene catalyzed by a $RhCl(CO)(PPh_3)_2$ solution and the isomerization of quadricyclene catalyzed by a Co(III)TPPCl solution were used to study the behavior of SLPC at low and high solubility, respectively. The experimental results were found to be in good quantitative agreement with the theoretical model for both cases.

1. INTRODUCTION

Ever since the potential applicability and the unique characteristics of supported liquid-phase catalysts (SLPC) were independently recognized by two investigators (*1*, *2*), a number of experimental investigations using the technique have been reported in the literature. The reactions studied include (a) isomerization of 1-pentene with $RhCl_3$ (*1*), (b) isomerization of 1-butene with $RhCl_3$ (*3*), (c) hydrogenation of propylene with $RhCl(PPh_3)_3$ (*3*), (d) hydroformylation of propylene with $RhCl(CO)(PPh_3)_2$ (*4*), (e) hydroformylation of propylene and ethylene with $RhHCO(PPh_3)_3$ (*5*), (f) oxidation of ethylene to acetaldehyde with aqueous solution of $PdCl_2$–$CuCl_2$ (*6*), (g) oxidation of carbon monoxide with $PdCl_2$–$CuCl_2$ (*7*), and (h) oxidation of sulfur dioxide with melts of V_2O_5–$K_2S_2O_7$ (*8*). The emphasis in most of the above studies was on experimental work. Thus far, only two investigators (*4*, *8*) have attempted to correlate their models, containing adjustable parameters, with experiments.

The objective of this investigation was to obtain experimental verification of our predictive model for transport and reaction of gaseous species in supported liquid-phase catalysts described in Part I (*9*) of this series.

2. CHOICE OF MODEL REACTIONS

Since the solubility of the gaseous reactants in the liquid phase is clearly a key parameter governing the behavior of SLPC systems, it was decided to study two different model reactions: one in the low solubility range and the other at the high solubility limit. The reactions chosen, respectively, are:

(a) the hydrogenation of ethylene catalyzed by *trans*-chloro-carbonyl bis(triphenyl phosphine) rhodium(I) dissolved in dioctyl phthalate with an excess of triphenyl phosphine, and (b) the valence isomerization of quadricyclene (C_7H_8) to norbornadiene catalyzed by chloro-meso-tetraphenyl porphyrinato-cobalt(III) in solution with 1-chloronaphthalene.

The ethylene hydrogenation reaction was chosen to study SLPC behavior at the low solubility limit because it is a simple reaction, the catalyst is relatively stable, there are no side reactions, and the reactants and product are all supercritical gases at the re-

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action conditions. The catalyst, *trans*-Rh $Cl(CO)(PPh_3)_2$, is a well-known hydroformylation catalyst and was reported (*10*) to catalyze the hydrogenation of ethylene in benzene or toluene at 310 to 330 K and 0.1 MPa, but the reaction was very slow. However, for our reaction conditions of 1.6 MPa (absolute) pressure and 393 K temperature, we found this catalyst to be very active. Dioctyl phthalate (DOP) was chosen as the solvent because of its very low volatility (1.6×10^2 Pa vapor pressure at 493 K).

The reasons for appropriateness of the quadricyclene isomerization as a model reaction for SLPC as well as its kinetics are given elsewhere (*11–13*). There is also some interest in this reaction as a promising system for photochemical solar energy storage through the sensitized photolysis of the reverse conversion of norbornadiene to quadricyclene (*14*). The catalyst, Co(III) TPPCl, is extremely active and is also very stable. The solvent chosen was 1-chloronaphthalene because of it low volatility.

3. EXPERIMENTS

(*a*) *Materials*

The ethylene hydrogenation catalyst, Rh $Cl(CO)(PPh_3)_2$, and the solvent DOP were purchased from Aldrich Chemical Company; the liquid, triphenyl phosphene, was obtained from MCB Manufacturing Chemists, Inc. The quadricyclene isomerization catalyst, Co(III) TPPCl, and the reactant quadricyclene were prepared in our laboratory (*11*, *15*). The porous support used, α-alumina T-708 (Table 1), 6×10^{-3} by 6×10^{-3} m cylindrical pellets, was obtained from the Girdler Catalysts Division of Chemetron Corporation. This support was also used in the study described in Part II (*16*). Its relevant physical characteristics are listed elsewhere (*17*). The gases used were purchased from Scientific Gas Products, Inc., and were high-purity dry grade.

TABLE 1

Physical Characteristics of Girdler T-708 α-Alumina Porous Support

Void volume, V_g	0.4717×10^{-3} m³/kg
Pore surface area, S_0	7.5×10^3 m²/kg
Average pellet thickness, $2L$	5.903×10^{-3} m
Average pellet diameter	5.982×10^{-3} m
Pellet density, ρ_p	1.5101×10^3 kg/m³
True density, ρ_s	5.249×10^3 kg/m³
Porosity (Hg porosimeter), θ^O	0.7123
Dusty-gas constants	
C_0^O	2.97×10^{-15} m²
C_1^O	3.27 Å
C_2^O	0.3892
σ	2.63

Note. Pore-size distribution data are given elsewhere (*17*).

TABLE 2

Operating Conditions for Hydrogenation of Ethylene in SLPC

$RhCl(CO)(PPh_3)_2$ conc.	5 mol/m³
Solvent	Dioctyl phthalate
PPh_3/Rh weight ratio	15/1
Temperature	393 K
Pressure (absolute)	1.6 MPa
Gas flow rate (STP)	1×10^{-6} to 3×10^{-6} m³/s
No. of pellets in reactor	8
Feed composition (molar)	
Ethylene	5%
Hydrogen	95%
Stirrer speed	1000 rpm

(*b*) *Catalyst Preparation*

For ethylene hydrogenation, RhCl $(CO)(PPh_3)_2$ and triphenyl phosphine were added to DOP in amounts required to prepare a stock solution with the concentration listed in Table 2, and the mixture was slowly heated for about 7×10^3 s to dissolve the solids. The work was performed under a nitrogen atmosphere and contact with air was minimized. It was discovered that the activity of the catalyst solution is dependent on the temperature to which it is heated during dissolution. However, reproducible activity was obtained by following the same procedure. The stock solution for quadricyclene isomerization catalyst was prepared by adding Co(III) TPPCl to 1-chloronaphthalene in amounts required to

TABLE 3

Operating Conditions for Isomerization of Quadricyclene in SLPC

Co(III)TPPCl concentration	2.46 × 10^3 mol/m^3
Solvent	1-Chloronaphthalene
Temperature	403 K
Pressure (absolute)	0.1 MPa
Gas flow rate (STP)	1 × 10^{-6} to 2 × 10^{-6} m^3/s
Feed composition (molar)	
Nitrogen	95%
Quadricyclene	5%
Stirrer speed	1000 rpm

obtain the concentration listed in Table 3. The mixture was then stirred for several hours to dissolve the solid. The resulting catalyst solutions were quite stable and could be stored for months without significant loss of activity.

The liquid-loaded pellets were prepared as follows: (a) the catalyst solution was dissolved in chloroform in a volumetric ratio corresponding to the desired liquid loading; (b) the pellets were kept under vacuum overnight; (c) the vacuum pump was then shut off and the catalyst solution was added, breaking the vacuum and immersing the pellets; (d) the pellets remained immersed in solution for 5 × 10^5 to 6 × 10^5 s; and (e) the pellets were finally removed from the solution and placed under vacuum for 3.6 × 10^3 s to remove the chloroform. The cobalt catalyst is a strong dye and, thus, it was confirmed by breaking open the pellets that full penetration of the catalyst solution in T-708 pellets was achieved by soaking for approximately 6 × 10^5 s. By following the weight loss of pellets under vacuum, it was also established that all the chloroform was dried off in about 900 s without any concomitant loss of the solvent DOP or 1-chloronaphthalene.

(c) *Apparatus and Procedure*

The specially constructed continuous-flow stirred reactor was fabricated from stainless steel (SS316) and equipped with a variable-speed Magnedrive assembly supplied by Autoclave Engineers. From residence-time-distribution studies accompanied by changes in the stirring speed, the mixing pattern in the gas phase very closely approximated perfect mixing.

Gas-feed mixtures entered the reactor at the top, around the packless magnetic drive shaft, and were removed at the bottom. Stainless-steel screens were used to retain the catalyst pellets. These were separated by Teflon spacers with a tight fit to avoid bypassing of the pellets by the gas. Analysis of the product stream was carried out periodically with an on-line HP5830 gas chromatograph.

In the present experiments, eight α-alumina T-708 pellets were mounted in a Teflon disk so as to seal off the cylindrical surface of the pellets, leaving only the flat end surfaces exposed to the gas. This was done so that infinite slab geometry could be assumed in the analysis. All experiments were performed with freshly prepared pellets. Linde mass flow meters provided accurate measurements and control of gas flow rates. A large excess of hydrogen (5% C_2H_4, 95% H_2) was maintained in the feed to ensure pseudo-first-order kinetics. The operating conditions for the ethylene hydrogenation experiments are summarized in Table 2. An average run lasted 4 × 10^4 to 5.5 × 10^4 s, although longer runs (up to 60 × 10^4 s) were conducted to check the stability of the rhodium catalyst. The activity varied somewhat with time, thus introducing some uncertainties in the results, but was relatively stable after a few hours. The conversion obtained for each run represents the average value of four to five measurements taken 3.5 × 10^4 to 4.5 × 10^4 s after starting the run.

The apparatus used for quadricyclene isomerization experiments was the same as that used for the ethylene hydrogenation experiments. The only modification was a sparging unit containing liquid quadricyclene and glass beads placed in the flow scheme immediately downstream of the mass flow meters. This permitted quadricyclene vapors to be fed to the reactor by sparging the carrier gas, nitrogen, through the sparging unit. The sparging unit was kept at 277 K by a constant-temperature bath equipped with a refrigeration unit. This was done to prevent vapors from condensing in the tubing. The operating conditions are summarized in Table 3. Experiments were performed in precisely the same manner as the ethylene hydrogenation runs. A typical run was of 11×10^3 s duration, although one run of 26×10^4 s was conducted to check catalyst stability. Each data point represents the average value of five measurements taken 7×10^3 to 11×10^3 s after beginning a run.

(*d*) *Liquid-Phase Kinetics*

Some experiments were also performed in the apparatus described above by placing a small glass dish containing a stagnant pool of the catalyst solution in the reactor in order to study the homogeneous liquid-phase kinetics. The quadricyclene isomerization reaction is first order in quadricyclene liquid-phase concentration and is essentially irreversible (*11*). The ethylene hydrogenation reaction was assumed to be pseudo first order in ethylene concentration for the feed-gas composition employed in the experiments. The first-order or pseudo-first-order rate constant, k_A, for either reaction was obtained from the liquid-pool experiments using the following analysis:

The gas phase in the reactor being well stirred, the external gas film resistance was estimated to be negligible. Then, for the quiescent liquid pool

$$f_A = \frac{1}{M\phi_L \tanh \phi_L + 1}, \tag{1}$$

where the Thiele modulus for the liquid pool is

$$\phi_L = \delta \sqrt{\frac{k_A}{D_A^L}} \tag{2}$$

and the dimensionless parameter

$$M = \frac{A_L H_A D_A^L}{F\delta}. \tag{3}$$

In the above equations, F is the volumetric gas flow rate, A_L is the surface area of the liquid pool, δ is its depth, and $f_A = C_{As}^G/C_{Ai}^G$ is the ratio of outlet to inlet concentration of A in the stirred reactor. All parameters in these equations are known except the rate constant, k_A, which can hence be calculated.

4. RESULTS AND DISCUSSION

(*a*) *Hydrogenation of Ethylene*

If we represent C_2H_4, C_2H_6, and H_2 by A, B, and C, respectively, then the hydrogenation reaction can be written as

$$A + C \rightarrow B.$$

For the reaction conditions, it was estimated using Eq. (6), Part I, that $dP/dz \rightarrow 0$; i.e., the pellet is essentially isobaric. For this system, the last term on the right-hand side of Eq. (8), Part I, is also negligible. Thus, the overall flux of A can be adequately described by Eq. (39), Part I, with the overall effective diffusivity of A taking the form

$$D_{Ae} = \frac{C_2^O(1-q)^2}{\dfrac{x_C}{D_{AC}} + \dfrac{x_B}{D_{AB}} - x_A\left(\dfrac{1}{D_{AC}} - \dfrac{1}{D_{AB}}\right) + \dfrac{1}{(1-q)^{1/3}D_{kA}}} + C_2^O H_A D_A^L q^2. \tag{4}$$

Further, since A and B are present in trace amounts in C under our experimental conditions, we may use average values for their mole fractions, thus yielding an invariant overall effective diffusivity. Then, for the slab geometry ($h = 0$) of SLPC pellets, the effectiveness factor from Eq. (42), Part I, reduces to the usual form

$$E_p = \frac{\tanh \phi_p}{\phi_p}, \tag{5}$$

where ϕ_p is given by Eq. (43), Part I.

The reaction velocity is obtained by rearranging Eq. (46), Part I, to give

$$\frac{r_A}{C_{As}^G} = L\theta^O q H_A k_A E_p. \tag{6}$$

The experimental reaction velocity is calculated by

$$\frac{r_A}{C_{As}^G} = \frac{F}{A_p}\left(\frac{1}{f_A} - 1\right), \tag{7}$$

where A_p is the total external surface area of SLPC pellets exposed to A in the stirred reactor.

The parameters used in the above equations are presented in Table 4 and were calculated as follows: The binary gas diffusion coefficients were calculated from the Chapman–Enskog formula (*18*); the Knudsen diffusion coefficients were calculated using Eq. (41), Part I; the liquid-phase diffusion coefficient was calculated using the Wilke–Chang equation (*19*); and the solubility (partition coefficient H_A) of ethylene was estimated from regular solution theory. The pseudo-first-order rate constant was obtained from the liquid-pool experiments described earlier.

In Fig. 1 the theoretical reaction velocity, calculated using Eq. (6) and the parameter values listed in Table 4, is plotted versus the liquid loading along with the experimental points. As predicted, the data verify a maximum in the reaction rate for an optimum liquid loading. The experimental points deviate somewhat from the theoretical curve, but the overall agreement is quite good considering that the model involves no adjustable parameters. All the parameters employed in the calculations were either theoretically estimated or independently obtained from experiments.

TABLE 4

Values of Constant Parameters Employed in the Calculations for Hydrogenation of Ethylene in SLPC

Parameter	Value
D_{AB}	0.301×10^{-6} m²/s
D_{AC}	5.90×10^{-6} m²/s
D_{kA}	4.58×10^{-5} m²/s
D_{kB}	4.43×10^{-5} m²/s
D_{kC}	1.71×10^{-4} m²/s
D_A^L	2.62×10^{-9} m²/s
H_A	0.40
k_A	0.40 s⁻¹

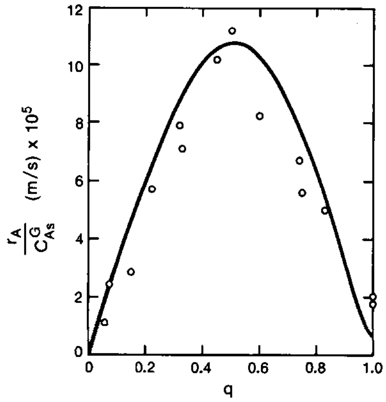

FIG. 1. Experimental points and theoretical reaction velocity curve for the hydrogenation of ethylene by RhCl(CO)(PPh$_3$)$_2$ in SLPC at 393 K and 1.6 MPa.

(b) Isomerization of Quadricyclene

Representing quadricyclene by A and the norbornadiene by B, the isomerization reaction can be written as

$$A \rightarrow B.$$

The reaction conditions are given in Table 3. Since A and B are present in small amounts compared to the inert I (carrier gas nitrogen), this case corresponds exactly to the illustrative example of Part I, and the expressions derived there are applicable.

The theoretical reaction velocity is plotted in Fig. 2 versus the liquid loading along with the experimental data. The parameter values employed in the calculations are listed in Table 5. They were obtained in the same manner as the corresponding parameters for the ethylene hydrogenation reaction, except for the partition coefficient, H_A, which was obtained independently from absorption experiments (*20*). The agreement between the theoretical curve and the experimental data is quite good.

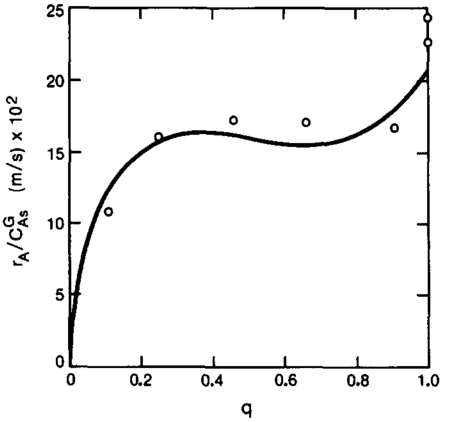

FIG. 2. Experimental points and theoretical reaction velocity curve for the isomerization of quadricyclene by Co(III)TPPCl in SLPC at 403 K and 0.1 MPa.

Note that as expected the maximum rate of reaction for this case is at full liquid loading owing to the high solubility of the reactant in the catalyst solution ($H_A = 350$).

It may be finally mentioned that our SLPC model (Part I) based on the original dusty-gas model can be easily modified to incorporate the refinement suggested in Part II on the basis of permeability experiments. However, this modification may not be necessary for many cases since, although the original dusty-gas model is apparently deficient in accounting for pressure-driven fluxes, this term is often negligible in reacting systems (*21*) as, for example, in the model reactions considered here (see also the arguments preceding Eq. (10), Part I).

5. CONCLUSION

We have described here experimental studies of both the high and low solubility limits for SLPC systems as represented by the isomerization of quadricyclene catalyzed by Co(III)TPPCl and the hydrogenation of ethylene catalyzed by RhCl (CO)(PPh$_3$)$_2$, respectively. The experimental results confirm the existence of a predicted maximum in the reaction rate of ethylene hydrogenation for an intermediate liquid loading while the maximum rate of reaction for quadricyclene isomerization is at full liquid loading. Clearly, the advantages of SLPC are most evident for systems of low solubility. The experimental results are in good overall agreement with the theoretical predictions. All parameters employed in the calculations were either evaluated theoretically or obtained by separate independent experiments. It can therefore be concluded that the theoretical model proposed in Part I for transport and reaction in supported liquid-phase catalysts involving catalytic liquids with contact angle less than 90° is quite adequate for quantitative predictions.

APPENDIX: NOMENCLATURE

Refer to the appendixes of Parts I and II. Additional symbols introduced in Part III are listed below.

A_L	gas–liquid interfacial area of liquid catalyst pool (m^2)
A_p	external surface area of SLPC pellets exposed to reactants (m^2)
C^G_{Ai}	gas phase concentration of A at the reactor inlet (mol/m^3)
F	volumetric gas flow rate through the reactor (m^3/s)
f_A	dimensionless concentration of A at the reaction outlet (C^G_{As}/C^G_{Ai})
L	half-thickness of the pellet (m)
M	dimensionless parameter for liquid pool defined by Eq. (3)

TABLE 5

Values of Constant Parameters Employed in the Calculations for Isomerization of Quadricyclene in SLPC

Parameter	Value
D^L_A	4.42×10^{-9} m^2/s
D_{AB}	2.72×10^{-6} m^2/s
D_{Ai}	8.77×10^{-6} m^2/s
D_{kA}	2.56×10^{-5} m^2/s
H_A	350
k_A	280 s^{-1}

V_g void volume of dry porous support per unit mass of pellet (m^3/kg)

Greek symbols

δ depth of liquid catalyst pool (m)
ρ_s true density of pellet material (kg/m^3)
ϕ_L Thiele modulus for liquid catalyst pool (Eq. (2), dimensionless)

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