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Kinetic Analysis of Diffusion-Disguised First-Order Reaction Systems with a Diffusion Reactor

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The applicability of the diffusion reactor for testing the activity and selectivity behavior of commercial catalysts is investigated with *n*-hexane isomerization and cracking on a bifunctional Pt/Al_2O_3 catalyst as a model reaction. It is demonstrated that the diffusion reactor is well suited for kinetic analysis of diffusion-disguised single reactions and first-order reaction networks as long as restrictions due to attained equilibrium concentrations in the centerplane chamber can be circumvented. The obtained product distributions from *n*-hexane and 2- and 3-methylpentane conversion are discussed in terms of underlying reaction mechanisms.

INTRODUCTION

The performance of industrial catalysts is quite often influenced by internal mass transport limitations. In laboratory studies of the kinetics of heterogeneous catalytic reaction systems with the aims of catalyst screening, and in scale-up from laboratory equipment to pilot plants and industrial plants and process optimization, these limitations need to be analyzed. This is usually done by measuring reaction rates at differing particle sizes under otherwise identical reaction conditions. The Thiele parameter and the effective diffusivity are then calculated from the relationship between the effectiveness factor and the particle size or from reaction rates over catalyst pellets with effectiveness factors close to unity and less than unity (*1*).

A further approach has been presented by Petersen and co-workers (*2–4*), who used a diffusion reactor which allows concentration measurements in the bulk fluid flow (either once-through flow or recycle flow) and in the center of the catalyst pellet for simultaneous determination of effective diffusivities and rate constants of chemical reactions. The applicability of the diffusion reactor for kinetic investigation of diffusion-disguised first-order reaction networks has been demonstrated by Herz and Hegedus (*5*) with a theoretical analysis based on the work of Wei and Prater (*6, 7*). One of the drawbacks of the diffusion reactor for testing commercial catalysts is the mode of preparation of the pellet by pressing pulverized catalyst into a cylindrical support ring. By this procedure the structure of the secondary pore system which usually mainly causes limitations of measured conversions by mass transport effects depends on press time and press pressure and may be different from the pore structure of the original catalyst pellets.

In the present investigation potential applications of the diffusion reactor for testing commercial catalysts are studied and exemplified with isomerization and cracking of *n*-hexane on a Pt/Al_2O_3 catalyst, which have been shown to follow first-order kinetics (*8*), as a model reaction. In particular, effective diffusivities and rate constants for *n*-hexane conversion are determined using catalyst pellets with different secondary pore structures. Furthermore, the kinetics of simultaneous interconversion of *n*-hexane and the methylpentanes and hydrogenolysis of the hexane isomers are investigated.

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EXPERIMENTAL

Materials. Kali-Chemie AG provided 0.35 wt% Pt/alumina catalyst (RD 150 C). *n*-Hexane and 2- and 3-methylpentane were purchased from Riedel-de Haen AG. Hydrogen was dried over molecular sieves to a content of less than 0.5 vpm H_2O.

Apparatus and operation conditions. The experiments were carried out in a diffusion reactor described earlier (*8, 9*). For the above indicated investigations three kinds of experiment are required. The determination of "physical" effective diffusivities on the basis of the dusty gas model (which accounts for d'Arcy flow, Knudsen and bulk diffusion through an isothermal porous medium) requires permeability and stationary counterdiffusion measurements. The experimental set-up and procedure for these measurements are given elsewhere (*9*).

For determination of effective diffusivities under reaction conditions and of the rate constants for interconversion of *n*-hexane and the methylpentanes a hydrogen carrier gas flow loaded with reactants by oversaturator/saturator systems is passed at one side of the catalyst pellet. Possible film diffusion effects were analyzed by use of the Chilton/Colburn criterion (*10*). Furthermore, different flow rates were adjusted during the counterdiffusion measurements and the data evaluated with respect to the effective binary diffusivity. As a result experimental gas velocities were applied at which film diffusion effects did not influence the measured effective binary diffusivities. On the opposite site of the cylindrical pellet a closed chamber is attached from which small samples for gas chromatographic analysis can be withdrawn with a syringe. The three saturators which contain *n*-hexane and 2- and 3-methylpentane can be cooled independently from each other, as a result of which the same partial pressures of individual reactants and reactant mixtures can be achieved. By means of a valve system the feed flow or the product flow can be passed through the sample loop of a six-port valve connected with a gas chromatograph (100 m squalane capillary column, flame ionization detector). Temperatures can be monitored on both sides of the catalyst pellet. Temperature gradients along the pellet did not exceed 1°C. One gram of catalyst powder (particle diameter 0.2 mm) was pressed at either 500, 1000, or 2000 bar into the cylindrical pellet holder, by which the center-plane chamber and the bulk fluid flow are separated.

Permeability and stationary counterdiffusion measurements were carried out at 20°C with a catalyst pellet pressed at 2000 bar using H_2 and H_2/*n*-hexane mixtures, respectively. Reaction conditions for simultaneous determination of effective diffusivities and rate constants for hexane conversion were 436°C, hexane partial pressure 10–80 Torr, carrier gas H_2, flow rate 100 ml/min (STP), total pressure 1050 Torr. The kinetic investigation of hexane/methylpentanes interconversions was carried out at an alkane partial pressure of 22 Torr, a total pressure of 1050 Torr, 335°C, on a catalyst pellet pressed at 500 bar (pellet diameter 12.9 mm, length 7.2 mm).

RESULTS AND DISCUSSION

Diffusivities and Rate Constants for Hexane Conversion on Pellets with Different Secondary Pore Structures

The applicability of the diffusion reactor for measuring rate constants of chemical reactions without diffusion disguise can be examined with conversion measurements using catalyst pellets with different secondary pore structures under otherwise identical reaction conditions.

For a first-order model reaction the analysis will be performed in the following way: the material balance for an isothermal catalyst pellet is given by

$$\frac{d^2\psi_A}{d\eta^2} = h_\lambda{}^2\psi_A \qquad (1)$$

with the boundary conditions

$$\psi_A = 1 \text{ at } \eta = 1; \qquad \frac{d\psi_A}{d\eta} = 0 \text{ at } \eta = 0.$$

The solution of this equation is

$$r_A = \frac{\tanh(h_\lambda)}{h_\lambda} \cdot k \cdot a_A(1)\pi R^2 L \qquad (2)$$

or in terms of the center concentration

$$\psi_A(0) = \frac{a_A(0)}{a_A(1)} = \frac{1}{\cosh(h_\lambda)} \qquad (3)$$

where ψ_A is a dimensionless concentration, R = pellet radius, L = length of the pellet, a_A = concentration of component A, $a_A(0)$ = centerplane concentration, $a_A(1)$ = bulk concentration, r_A = overall reaction rate, h_λ = Thiele modulus = $L(k_1/D_{\text{eff}})^{1/2}$, $\eta = y/L$, y = position variable. D_{eff} is based on the total cross-section normal to diffusion direction and is defined as the ratio of the flux through this cross-section to the concentration gradient.

From a measurement of the concentration in the bulk phase and the corresponding centerplane concentration the Thiele modulus is obtained (Eq. (3)) and with knowledge of the overall reaction rate in the bulk phase the effective diffusivity can be computed from the Thiele modulus. In Table 1 rate constants for *n*-hexane conversion, which are computed from conversion measurements in the bulk phase at different *n*-hexane partial pressures and effective diffusivities, are presented for three pellets pressed at different total pressures.

As the results reveal, with increasing press pressure during preparation of the pellet the effective diffusivity decreases from 0.029 to 0.014 cm²/s, whereas within experimental error the same rate constant for *n*-hexane conversion is obtained.

In order to prove the significance of the effective diffusion coefficients obtained under reaction conditions the effective diffusivity under nonreactive conditions was determined by means of permeability and stationary counterdiffusion measurements on the basis of the dusty gas model (*11*). The results with pellet 3 are given in the following:

$$D_{\text{K, eff, H}_2\text{, 293°K}} = 0.019 \text{ cm}^2/\text{s};$$

$$D_{\text{12, eff, }n\text{-C}_6\text{/H}_2\text{, 293°K}} = 0.042 \text{ cm}^2/\text{s}.$$

From the known temperature and molecular weight dependences of these diffusivities and by use of the Bosanquet equation the following diffusivity $D_{\text{eff, 430°C}} = 0.02$ cm²/s is obtained, which agrees well with the effective diffusivity under reaction conditions.

Kinetic Analysis of n-Hexane/Methylpentanes Interconversion

The change of composition of *n*-hexane/methylpentanes interconversion with time in a diffusion reactor can be represented by the following set of differential equations:

$$\nabla^2 \alpha - [(L^2 a) D^{-1} K]\alpha = 0 \qquad (4)$$

TABLE 1

Influence of Press Pressure on Effective Pellet Diffusivities and Rate Constants

Pellet number	Press pressure (bar)	Weight (g)	Length (mm)	Porosity	BET-area (m²/g)	Rate constant[a] (s⁻¹)	D_{eff} (cm²/s)
1	500	1	7.2	0.72	349	0.49	0.029
2	1000	1	6.78	0.7	369	0.47	0.019
3	2000	1	6.29	0.67	367	0.44	0.014

[a] Reaction conditions: reaction, *n*-hexane → isohexanes + cracking products, 436°C; total pressure, 1050 Torr; *n*-hexane partial pressure, 10–80 Torr; carrier gas, hydrogen; carrier gas velocity, 100 ml/min (STP).

where $\alpha = \begin{bmatrix} n\text{-hexane} \\ 2\text{-methylpentane} \\ 3\text{-methylpentane} \end{bmatrix}$ is the composition vector, K is the rate constant matrix, D is the diagonal matrix of the effective diffusivities, a the catalytic active area per unit volume of pellet [cm^2/cm^3], and L the thickness of the pellet. With the boundary conditions $\nabla\alpha = 0$ at $\eta = 0$ and $\alpha = \alpha(1)$ at $\eta = 1$ the solution is:

$$\alpha(0) = X[1/\cosh(h_\lambda)]X^{-1}\alpha(1) \qquad (5)$$

where X and $h_\lambda{}^2$ are the eigenvectors and the eigenvalues of the matrix $[(L^2a)D^{-1}K]$.

According to Herz and Hegedus (*5*) Eq. (5) may be rewritten by introducing the concentration matrices $C(1)$ and $C(0)$ formed from the single bulk and centerplane concentration column vectors instead of the composition vectors $\alpha(1)$ and $\alpha(0)$. Multiplying from the right by the inverse of $C(1)$ and the eigenvector matrix X the following equation is obtained:

$$[C(0)C(1)^{-1}]X = X[1/\cosh(h_\lambda)]. \qquad (6)$$

Thus from the experimentally determined matrix $[C(0)C(1)^{-1}]$ the eigenvectors and eigenvalues are computed by which the eigenvector matrix X and after calculation from $[1/\cosh(h_\lambda)]$ the eigenvalue diagonal matrix of the original matrix $[(L^2a)D^{-1}K]$ are obtained. The rate constant matrix and the diffusivity matrix can be separated by making use of the reaction rates measured simultaneously with corresponding sets of bulk and centerplane concentrations in the bulk phase. For the present reaction system the effective diffusivities may be assumed equal for the individual reactants and the relative values of the rate constants are directly obtained from $[D^{-1}K]$.

A limitation in applicability of the diffusion reactor is that in the closed centerplane chamber thermodynamic equilibrium concentrations may be obtained, even though starting from different initial compositions at a certain reaction temperature. This situation will always be found in the case of small diffusivities as compared to corresponding reaction rate constants. In these cases a kinetic analysis of reaction systems is no longer possible. Mathematically the matrix $[C(0)]$ then has the rank 1 and therefore the matrix $[C(0)C(1)^{-1}]$ too and all eigenvalues are zero except one. These difficulties can be circumvented by lowering the reaction temperature or by reducing the thickness of the pellet.

A lowering of the reaction temperature, however, may not be suitable, especially with complex reaction systems, because the reaction mechanism by which the reactants are transformed into products may change. This is the case with the present reaction system (*12, 13*). Above ca. 430°C products are mainly formed via a bifunctional mechanism, where platinum displays only (de)hydrogenation activity and skeletal rearrangements of the hydrocarbons occur on the acidic sites and large amounts of dimethylbutanes are observed among the products. Below ca. 400°C mainly platinum reactions contribute to the measured product distributions. In this case only small amounts of dimethylbutanes are observed among the products, because dimethylbutane formation from methylpentanes is a slow reaction on platinum. Enlargement of the catalyst pellet is also restricted.

A further drawback concerns the analysis of Herz and Hegedus (*5*). Contrary to the analysis of Wei and Prater (*7*), where the eigenvectors and eigenvalues of the rate constant matrix are individually determined by sets of experimental data, the set of eigenvectors and eigenvalues is computed from the experimental matrix $[C(0)C(1)^{-1}]$. Thus these eigenvectors and eigenvalues are correlated with each other through experimental, model, and numerical errors and the physical significance of the corresponding rate constants may hardly be recognized.

The procedure described above is used in the following for kinetic analysis of n-hexane/methylpentanes interconversion and hydrogenolysis. The matrix comprised of the single bulk phase composition vectors at the reactor exit is given by:

$$\begin{vmatrix} 0.0125 & 0.0092 & 0.5349 & 0.9553 & 0.3187 & 0.0091 \\ 0.0202 & 0.9574 & 0.4301 & 0.0103 & 0.0145 & 0.4395 \\ 0.9425 & 0.0098 & 0.0076 & 0.0067 & 0.6431 & 0.5277 \end{vmatrix}$$

The corresponding matrix of centerplane compositions is given by:

$$\begin{vmatrix} 0.0887 & 0.1064 & 0.3109 & 0.5671 & 0.2044 & 0.0832 \\ 0.1567 & 0.5794 & 0.3617 & 0.1373 & 0.1311 & 0.3358 \\ 0.5067 & 0.0927 & 0.0801 & 0.0647 & 0.4367 & 0.3595 \end{vmatrix}$$

Multiplying both matrices by the transpose of the matrix $[C(1)]$ and calculating the eigenvectors and eigenvalues of the matrix $[C(0)C(1)^{-1}]$ with a library program the following eigenvalues and eigenvectors are obtained: $\lambda_1 = 0.788$, $\lambda_2 = 0.506$, $\lambda_3 = 0.467$.

$$X = \begin{vmatrix} 0.45690 & -0.65039 & -0.45709 \\ 0.74591 & -0.09398 & 0.80729 \\ 0.48462 & 0.75376 & -0.37331 \end{vmatrix}$$

Relative rate constants calculated from these eigenvalues and eigenvectors are given in Fig. 1.

Calculated and experimental reaction paths are shown in Fig. 2, where the reaction paths have been projected onto the reaction plane of the reversible three-component system *n*-hexane, 2-methylpentane, 3-methylpentane in the coordinate system of the pure components. As the results reveal, there is good agreement between calculated and measured reaction paths, which signifies the applicability of the parameter estimation procedure described so far at least with respect to the aims claimed in the Introduction.

Due to the low reaction temperature at which the reactions were performed only platinum reactions contribute to the measured product distributions. The alumina carrier of the catalyst used displays no activity for skeletal rearrangement of hydrocarbons at this temperature (*12*). Hydrogenolysis reactions of *n*-hexane and the two methylpentanes proceed at nearly the same rate (Fig. 1). The obtained C_1–C_5 product distributions clearly indicate single cleavages of the C–C bonds in the feed hydrocarbons (Fig. 3). This result is in agreement with earlier results of hydrocarbon conversions on platinum black and on an acidic Pt/Al_2O_3 catalyst (*12*), where it has been shown that the *n*-hexane and methylcyclopentane hydrogenolysis selectivity of platinum drastically changes at a reaction temperature of ca. 400°C from single C–C bond cleavages to preferred multiple ruptures of terminal C–C bonds, due to carbonaceous deposits on the platinum.

Some remarks with respect to underlying isomerization mechanisms can be derived from observed isomer ratios in the centerplane chamber and at the reactor exit,

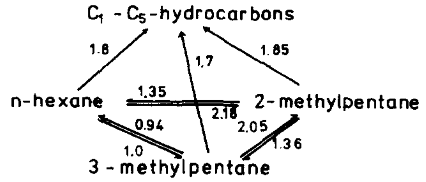

FIG. 1. Relative rate constants for isomerization and hydrogenolysis of *n*-hexane and the methylpentanes.

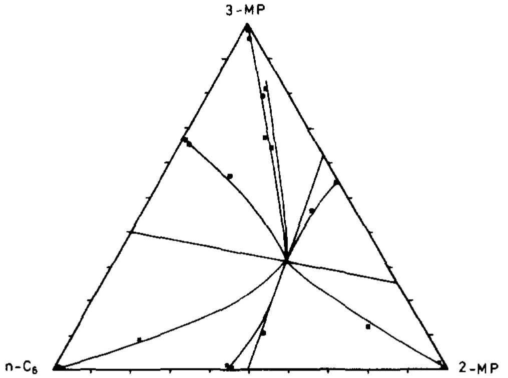

FIG. 2. Comparison of calculated (solid lines) and experimental reaction paths.

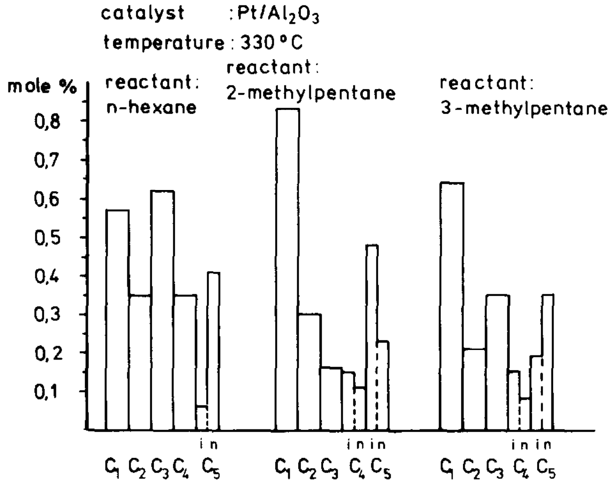

FIG. 3. Distribution of hydrogenolysis products obtained from *n*-hexane and 2- and 3-methylpentane conversion.

which, purged of feed impurities, are given in Table 2. The 2-/3-methylpentane ratio from *n*-hexane conversion amounts to 2.1, the *n*-hexane/3-methylpentane ratio from 2-methylpentane conversion to 1.1, and the *n*-hexane/2-methylpentane ratios from 3-methylpentane conversion to 0.6. There are some difficulties in fitting these results with the product distributions expected from isomerization mechanisms discussed in the literature (*14, 15*). It is generally accepted that skeletal isomerizations of alkanes proceed via different cyclic intermediates, either a cyclopropane configuration attached parallel to the catalyst surface (*16*), a metallocyclobutane structure (*14*), or a metallocyclohexane/metallocyclohexene structure (*14*). The first two mechanisms are usually termed the "bond shift" mechanisms, and the last one the "cyclic" mechanism. There is still discussion on the ensemble requirement for the single steps of the sequences of elementary steps through which skeletal rearrangements proceed and for the rate-determining steps of the different mechanisms (*15*). The cyclic mechanism, for example, may involve dicarbene intermediates formed with only one surface metal atom or dicarbyne/dicarbene intermediates formed with two surface metal atoms.

TABLE 2

Isomer Ratios from *n*-Hexane and 2- and 3-Methylpentane Conversion[a]

Reactant	Mole ratio of formed C_6 isomers[b]					
	2-MP/3-MP		n-C_6/3-MP		n-C_6/2-MP	
	RE	CP	RE	CP	RE	CP
n-Hexane	2.1	2.12				
2-MP			1.15	1.15		
3-MP					0.64	0.56

[a] Abbreviations: RE, reactor exit; CP, centerplane chamber; M, methyl; P, pentane.

[b] Reaction conditions: 335°C; total pressure, 1050 Torr; hydrocarbon partial pressure, 22 Torr.

With regard to the present results on the used platinum catalyst with high platinum dispersion, the isomer ratio obtained from *n*-hexane conversion fits quantitatively to product distributions expected from the "cyclic" mechanism with statistical C–C bond ruptures of the methylcyclopentane intermediate. However, the isomer ratios, obtained from 2- and 3-methylpentane conversion, can neither be associated with the "cyclic" mechanism nor with only one of

TABLE 3

Cyclization Products from *n*-Hexane and 2- and 3-Methylpentane Conversion

Reactant	Centerplane chamber concentrations[a] (mole%)		Bulk flow concentrations[a] (mole%)	
	MCP	Benzene	MCP	Benzene
n-Hexane	1.3	2.1	0.21	0.16
2-MP	1.6	0.6	0.23	—
3-MP	1.2	0.7	0.2	—

[a] Reaction conditions, see Table 2; MCP, methylcyclopentane.

the mechanisms described above, although the experimental runs were performed under the same experimental conditions as *n*-hexane conversion. Thus different mechanisms must "contribute" to the observed product distributions, the portion of which, however, cannot even be estimated, because most of these mechanisms have been introduced on the basis of occurrence or nonoccurrence of reactions of model compounds on different metal surfaces and little is known on the stability of the postulated intermediates. This knowledge, however, is a presupposition for quantitative precasting of product distributions assuming certain mechanisms.

Some results concerning cyclization and aromatization of the three hexane isomers are listed in Table 3. Nearly equal amounts of methylcyclopentane are formed from the three reactants not only in the bulk flow but also in the centerplane chamber. On the other hand no benzene is observed in the bulk flow from 2- and 3-methylpentane conversion, and a much larger amount from *n*-hexane conversion than from methylpentane conversions in the centerplane chamber. These results clearly indicate different aromatization routes of the feed hydrocarbons on the platinum catalyst via direct 1,6-ring closure and via 1,5-ring closure/ring expansion. If the 1,5-ring closure/ring expansion route would be the only operative aromatization mechanism equal amounts of benzene should be formed from the different reactants because equal amounts of methylcyclopentane have been observed. For discrimination among the two direct 1,6-ring closure mechanisms which are discussed in the literature, the alkatriene/cyclohexadiene route (*17*) and the route via 1,5,6-threepoint attached intermediates (*14*), further experimental data with specific model compounds are required.

CONCLUSIONS

The applicability of the diffusion reactor for kinetic analysis of diffusion-disguised first-order reaction systems has been demonstrated. The main experimental difficulties arise from a proper choice of contact times of reactants passing the catalyst surface in the bulk flow and diffusion times through the catalyst pellet, which is particularly a problem on catalysts with high activity and low diffusivity. Product distributions from platinum-catalyzed *n*-hexane and 2- and 3-methylpentane conversions have been compared with product distributions expected from mechanisms discussed in the literature, with a view to discriminating among rival mechanisms. This procedure, however, turned out to be rather restricted, because most of the literature mechanisms have been introduced on the basis of occurrence or nonoccurrence of model compound reactions on different metal surfaces and little or nothing is known about the stability of the proposed surface intermediates.

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