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Professor Joseph Joffe made the fugacity coefficient calculations on the ammonia/hydrogen and ammonia/propane binaries and compared them with the measurements of Antezana and Cheh (1975, 1976). He also made the calculations on the hydrogen sulfide/water binary. The author is also grateful to Robert H. Johnston for his helpful comments and to Exxon Research and Engineering Company for the permission to publish this paper.

NOTATION

a, b = parameters of polar contribution term to B, $f^{(2)}$; see Equation (4)
B = second virial coefficient
$f^{(0)}, f^{(1)}, f^{(2)}$ = dimensionless terms of Equation (3)
k_{ij} = characteristic binary constant; see Equation (6)
P = pressure
R = gas constant
$t(T)$ = (absolute) temperature
v = molar volume
y_i = vapor mole fraction of component i
z = compressibility factor
μ = dipole moment
ϕ_i = fugacity coefficient of component i
ω = acentric factor

Subscripts

c = critical property
i, j = property of component i, j
ij = characteristic property used in the calculation of the second virial cross coefficient
M = mixture property
R = reduced property

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Reaction Kinetics in Porous Electrocatalysts

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Porous electrocatalytic electrodes offer a high surface area and high activity for current generation, electrochemical processing, and investigation of catalytic surface reactions. However, slow reactant diffusion in the electrode pores can decrease the local reaction rate and can result in apparent experimental electrode-kinetic parameters (rates, orders, and transfer coefficients) which mask the true, intrinsic ones.

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Mathematical analyses and modeling of porous catalytic electrodes usually assume first-order electrochemical reactions to obtain expressions for electrode polarization in the presence of slow pore diffusion (DeLevie, 1967). Demonstrations of the adequacy of proposed models are often hampered by the complicated nature of the inherent kinetics of investigated reactions, for example, hydrocarbon fuel cell reactions. Because of this and the lack of knowledge about the dependence of catalytic activity on surface structure and morphology, few kinetic studies with porous electrocatalysts have been undertaken.

In this work we examine theoretically and experimentally the effect of pore diffusion on the electrode kinetics of nonfirst-order reactions. Such reactions often occur in the electrochemical reduction or oxidation of hydrocarbons on polytetrafluoroethylene bonded electrodes. A simple pore model (Austin, 1963; Srinivasan et al., 1967) was used here to describe reaction in the pores of a partially wettable electrocatalyst. The simplicity of this model permits ready analysis and allows a direct comparison with models for conventional heterogeneous catalysts using slab geometry (Aris, 1969). It can be shown that the more realistic models of Will (1963) and of Giner and Hunter (1969) would yield similar kinetic parameters.

The model consists of a catalytic slab with parallel pores partially filled with electrolyte. Figure 1 shows schematically a single simple pore. A dynamic gas-liquid-solid interface is formed in the pores. Reactant gas diffuses into the pores, dissolves in the electrolyte, and further diffuses in solution to reach the catalytic sites on the pore walls. Reactant electrolyte ions diffuse into the pore from the opposite side, and reaction occurs on the catalyst surface. Only slow axial diffusion is considered here. With thin electrodes, ohmic losses in the pores are small (Pshenichnikov et al., 1972); thus, constant potential is assumed in this treatment. Catalytic activity is also assumed to be constant along the pore.

For a j^{th} order irreversible electrochemical reaction, a steady state mass balance for species J in the electro-active part of the pore gives

$$\mathcal{D}_J \frac{d^2C_J}{dX^2} - \frac{2}{R_p}\overleftarrow{r}_J = 0 \qquad (1)$$

where $\overleftarrow{r}_J$ is the local intrinsic reaction rate

$$\overleftarrow{r}_J = \frac{\overleftarrow{i}_x}{nF} = k_J{}^0\, C_J{}^j \exp\left(-\,\alpha\, EF/\mathcal{R}T\right) \qquad (2)$$

Here $k_J{}^0$ is an Arrhenius type of rate constant at zero potential. Combining Equations (1) and (2) and writing them and the appropriate boundary conditions in dimensionless form, we obtain

$$\frac{d^2\theta_J}{dX^{*2}} - h^2\,\theta_J{}^j = 0 \qquad (3)$$

$\theta_J = 1$ at $X^* = 0$ (solution side);

$$\frac{d\theta_J}{dX^*} = 0 \quad \text{at} \quad X^* = 1 \qquad (4)$$

where $\theta_J = C_J/C_{J\infty}$, $X^* = X/L$, and

$$h = L\left[\frac{2k_J{}^0\, C_{J\infty}{}^{j-1}}{\mathcal{D}_J\, R_p}\exp\left(-\frac{\alpha EF}{RT}\right)\right]^{1/2} \qquad (5)$$

Similar to heterogeneous catalysis, the dimensionless group h is an electrochemical Thiele modulus. Here, h depends not only on concentration but also on the electrode potential.

Explicit analytic solution of Equations (3) and (4) is possible in simple cases, such as first-order (Austin, 1963; Srinivasan et al., 1967) and zero-order reactions (Sakellaropoulos and Langer, 1977). To simplify general analysis, an electrochemical effectiveness factor ϵ can be introduced to describe the observed current density (rate) i_g in terms of the intrinsic one i_∞. In analogy to conventional porous catalysts (Petersen, 1965), we obtain

$$\overleftarrow{i}_g = \overleftarrow{i}_\infty\,\epsilon = -\frac{\overleftarrow{i}_\infty}{h^2}\left(\frac{d\theta_J}{dX^*}\right)_{X^*=0} = \frac{\sqrt{2}}{h}\left[\int_0^1 \overleftarrow{i}_x(\theta)\,d\theta\right]^{1/2} \qquad (6)$$

or

$$\overleftarrow{i}_g = 2\pi R_p L N_p\, nFk_J{}^0\, C_{J\infty}{}^j\,\epsilon \exp\left(-\,\alpha EF/\mathcal{R}T\right) \qquad (7)$$

Obviously, ϵ depends on the potential. For slow pore diffusion as compared to reaction ($h_J \rightarrow \infty$), an asymptotic solution gives

$$\epsilon = \left(\frac{2}{j+1}\right)^{1/2}\cdot\frac{1}{h}$$
$$= \frac{1}{L}\left[\frac{\mathcal{D}_J R_p}{(j+1)\,k_J{}^0 C_{J\infty}{}^{j-1}}\exp\left(\frac{\alpha EF}{\mathcal{R}T}\right)\right]^{1/2} \qquad (8)$$

Thus, from Equations (7) and (8), the asymptotic kinetic parameters, indicated by primes, are related to the intrinsic ones by

$$\left.\begin{aligned} &\alpha' = \frac{\alpha}{2};\quad j' = \frac{j+1}{2};\quad k_J{}^0 \propto \sqrt{k_J{}^0} \\ &E_A' = \frac{1}{2}E_A = \frac{1}{2}\quad (\Delta H_o{}^{\neq} + \alpha\, FE) \end{aligned}\right\} \qquad (9)$$

Equations (7) and (8) predict that the Tafel slope ($2.3RT/\alpha F$) of an electrode reaction will double in the presence of slow pore diffusion for any reaction order. Also, the position of the current density-potential curve will be shifted from its initial position because of the concentration dependence of current. Previous treatments for first-order reactions did not predict position shifting.

To test the above model, simple gaseous olefins (ethylene through butylene) and liquid benzene were hydrogenated electrogeneratively on polytetrafluoroethylene bonded porous electrodes, activated with 9 mg/cm^2 platinum or palladium black. Experimental details for olefin hydrogenation were presented previously (Langer and Sakellaropoulos, 1975). The kinetic rate expressions and some kinetic parameters are given in Table 1. Because of the simple nature of the olefin reactions, it is easily verified that intrinsic reaction kinetics are observed on platinum and, for $P_{C_2H_4} > 0.3$ atm, on palladium. The reactions are

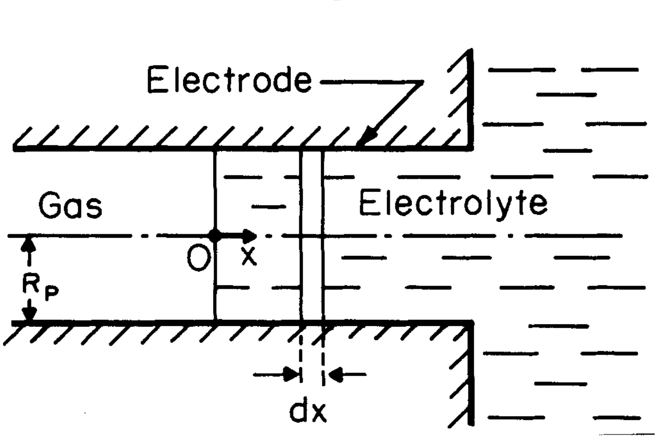

Fig. 1. Schematic representation of a simple pore.

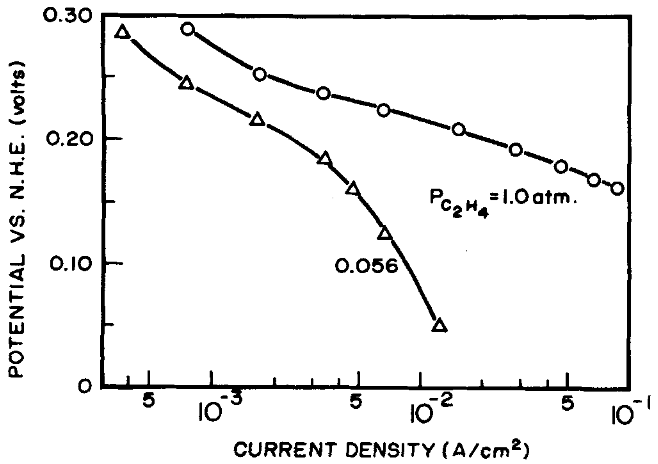

Fig. 2. Effect of gas phase concentration on the electrocatalytic kinetics of ethylene hydrogenation on palladium-black in 2N $HClO_4$, 25°C. ○—$P_{C_2H_4}$ = 1 atm; △—0.056 atm.

zero order in ethylene, probably owing to strong ethylene adsorption on the catalysts.

The reaction order in ethylene and the transfer coefficients on palladium suggest the onset of slow pore diffusion with decreasing ethylene partial pressure and potential. Figure 2 shows the change in the position and in the slope of the potential-current density curve as anticipated from Equations (7) to (9). With zero intrinsic kinetics observed at 1 atm of ethylene, electrochemical effectiveness factors at other partial pressures can be calculated at constant potential and H^+ concentration from the observed reaction rates (current densities) at pressure P and 1 atm, i_P and i_1, respectively:

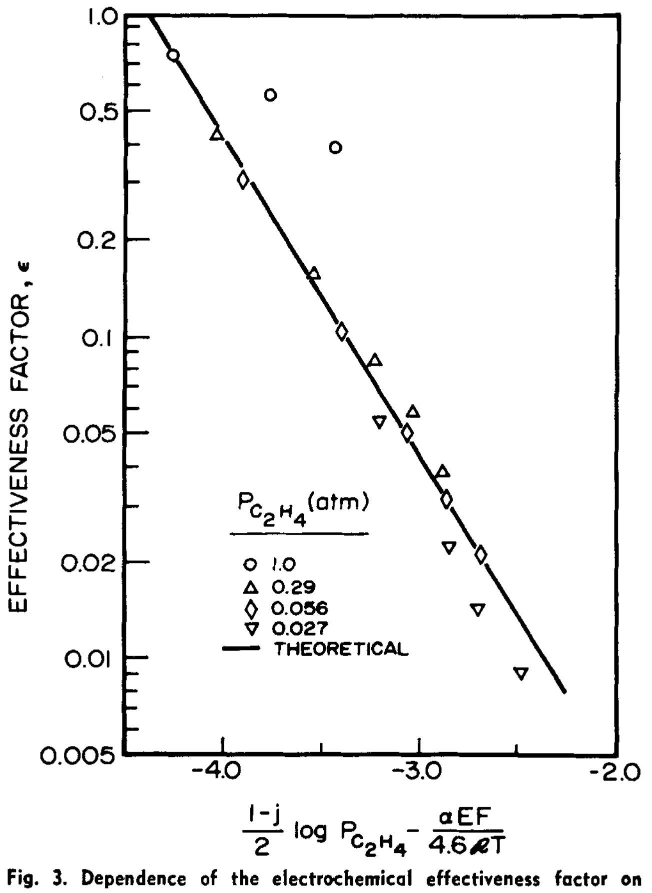

Fig. 3. Dependence of the electrochemical effectiveness factor on concentration and potential. Ethylene hydrogenation on palladium-black in 2N $HClO_4$, 25°C.

TABLE 1. EXPERIMENTAL KINETIC PARAMETERS FOR ETHYLENE AND BENZENE ELECTROCATALYTIC REDUCTION

	Ethylene*				Benzene*	
	Platinum		Palladium		Platinum	
	High E	Low E	High E	Low E	High E	Low E
Order in Substrate, e	0.1	0.1	0	0.4	0	—
Order in H⁺, h	1.9	1.9	1.8	1.8	1.8	1.45
Transfer coefficient, α	1.70	1.70	1.78	0.82	2	1
Tafel slope	0.035	0.035	0.033	0.072	0.029	0.059

* Reaction rate, $i = nFk_o C_E{}^e C^h{}_{H+} \exp(-\alpha EF/RT)$. Anode: platinum-black/hydrogen-gas.

$$\epsilon_{E,H^+} = \left(\frac{i_{g,p}}{i_\infty}\right)_{E,H^+} = \left(\frac{i_p}{i_1}\right)_{E,H^+} \tag{10}$$

Figure 3 shows the dependence of the experimental effectiveness factor on the variables, that is, electrode potential and partial pressure, as predicted by Equation (8). The theoretical line was calculated from Equation (8) using previously accepted values of L, $\mathfrak{D}_J$, and $k_J{}^0$ (Sakellaropoulos and Langer, 1977) and assuming a pore radius of about 50 μ for palladium. Experimental and theoretical results are in good agreement. Some data scattering probably reflects differences in the electrolyte penetration or wetting of the pores, the existence of a range of pore sizes, and possible change of reactant diffusivity with concentration in the electrolyte.

The model was also tested for ionic diffusion into the pores. In this case, ion diffusion occurs in the minus x direction, entering at $X^* = 1$, and similar equations hold as above.

Hydrogen ion pore diffusion does not develop in ethylene hydrogenation (Langer and Sakellaropoulos, 1975), but it is evident in benzene reduction on platinum-black electrodes. Liquid benzene was hydrogenated electrogeneratively in a horizontal cell with the platinum electrocatalyst placed at the electrolyte-benzene interface. The reaction rate equation and the kinetic parameters for this reaction are shown in Table 1. Both the transfer coefficient and the order in H^+ change with increasing current as predicted by Equation (9). Such evidence of Tafel slope change at high rates is rarely observed in fuel cell investigations. Slow pore diffusion of hydrogen ions in benzene reduction is probably caused by the wettability of platinum by the reactant and by strong benzene adsorption. These may cause steric hindrance to hydrogen ion diffusion at the pore entrance.

CONCLUSION

Simple reactions, such as ethylene or benzene electrogenerative hydrogenation, show that the electrode kinetic behavior of porous electrocatalysts can be predicted by a simple pore model. The theoretical and experimental analyses demonstrate that partially wettable porous catalytic electrodes behave kinetically similar to conventional catalysts in the presence of slow pore diffusion. Kinetic studies on porous electrocatalysts can, therefore, be meaningful and should be encouraged for catalyst characterization and for the design of electrochemical reactors.

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NOTATION

C = concentration, mole/cm^3
$\mathfrak{D}_J$ = diffusivity of species J, cm^2/s
E = electrode potential vs. N.H.E., Volts
E_A = activation energy, Joule/mole
F = Faraday's constant, A·s/equiv
$\Delta H_o^{\neq}$ = activation enthalpy, Joule/mole
h = electrochemical Thiele modulus
$\bar{i}$ = current density, A/cm^2
j = reaction order of species J
k_J^0 = rate constant at zero potential, mole^{1-j}·cm^{3j-2}·s^{-1}
L = electroactive pore length, cm
N_p = number of pores per unit area
n = number of electrons
R_p = pore radius, cm
$\mathcal{R}$ = gas constant, Joule/mole °K
$\bar{r}_J$ = reaction rate of species J, mole/cm^2·s
T = temperature, °K
X = axial distance, cm

α = transfer coefficient
ϵ = electrochemical effectiveness factor

$$= -\frac{1}{h^2}\left(\frac{d\theta_J}{dX^*}\right)_{X^*=0}$$

θ = dimensionless concentration $(= C_J/C_{J\infty})$

Subscripts

g = observed value, Equation (6)
J = species J
∞ = intrinsic or bulk solution value

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Restricted Diffusion of Liquids in Microporous Catalysts

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The problem of diffusion of liquid molecules in microporous catalysts and other porous material remains a difficult one in terms of relating effective diffusivities with the variables involved. Though there is a general concensus that there is a hindrance to transport of molecules in pores of finite width, the mechanisms contributing to this hindrance are not well understood. Even diffusivity data for molecules in porous media, though few in number, generally vary in magnitude because of the different set of assumptions and conditions under which experimental transport data are analyzed, and also due to difficulties in obtaining reliable measurements of low concentrations, very often in parts per million.

Several groups of workers have attempted to derive quantitative expressions for hindered diffusion in pores. Ferry (1936) proposed that hindered diffusion occurs because of the exclusion of molecules due to statistical effects related to the relative size of molecules to the pore. Ferry pictured the molecule as being reflected from the pore mouth if it is within a distance of less than one molecular radius from the pore wall. Recent theories (Ackers, 1970) derived from ideas in exclusion gel permeation chromatography related hindered diffusion to the exclusion phenomenon, which simply states in geometric terms that the equilibrium partition coefficient is given by

$$K_p = C_p/C_o = (1 - \lambda)^2 \qquad (1)$$

The geometric exclusion hypothesis neglects the very real effect of surface adsorption within the pore or the opposite effect of repulsion between molecule and surface. The magnitude of the adsorption or repulsion depends on the chemical and electrical properties of the surface and the solute molecules.

Subsequent efforts in development of a model to describe hindered diffusion was done by postulating a hydrodynamic drag effect (Friedman and Kramer, 1930; Faxen, 1973; Lane, 1950). However, neither of these adequately explained the reduction in effective diffusivity through porous material. Pappenheimer et al. (1951) and Renkin (1954) suggested the combination of the two effects to give

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