A Chemical Probe for Catalyst Nonuniformity

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Introduction

This note reports the results of an experimental study of diffusion and reaction in a catalyst particle that has a radial profile of active ingredient (Pt) described by the function $m(1-x)^{\alpha}$. The deuterium-neopentane exchange (DNE) reaction was employed in the study (Dwyer et al., 1968; Ernst and Daugherty, 1978; Ernst and Wei, 1975). The theory is based upon the work of Wei and Prater (1962) and Wei (1962a, b).

Ernst and Daugherty (1978) showed that the highly coupled system of rate equations which describe the behavior of D-exchanged hydride species such as neopentane can be uncoupled if the following transformation is made.

$$\boldsymbol{a} = \boldsymbol{X}\,\boldsymbol{b} \tag{1}$$

In this equation $\boldsymbol{b}$ is a vector of "characteristic" species b_i which are linear combinations of D-exchanged hydride mole fractions, a_i, and $\boldsymbol{X}$ is the matrix of eigenvectors of the rate constant matrix $\boldsymbol{B}$. In a batch reactor the rate of change of b_i in the gas phase can be expressed in matrix form

$$\frac{d\boldsymbol{b}}{dt} = -\bar{k}\,\boldsymbol{\Lambda}^{+}\,\boldsymbol{b} \tag{2}$$

as long as the surface reaction involves a single-step exchange process with negligible desorption (or β) effects. In elemental form, this equation becomes

$$\frac{db_i}{dt} = -\bar{k}\,i\eta_i\,b_i \tag{3}$$

and has the general solution

$$\frac{b_i}{b_i^{o}} = e^{-\bar{k}\,i\eta_i t} \tag{4}$$

Wang and Varma (1980) solved the intraparticle diffusion-reaction problem for a catalyst pellet that has an activity profile described by the equation $k(x) = m\bar{k}(1-x)^{\alpha}$. Their solution,

$$\eta_i = 3m\left[\frac{(\alpha+2)^{\alpha p}}{\phi_i^{2g} m^{g}}\frac{\Gamma(g)}{\Gamma(p)}\frac{I_{-p}(2pm^{1/2}\phi_i)}{I_p(2pm^{1/2}\phi_i)} + \frac{1}{\phi_i^2 mp}\frac{\Gamma(g)}{\Gamma(-p)}\right] \tag{5}$$

can be used to calculate the effectiveness factor for each b_i species if the Thiele modulus is defined as $\phi_i = R\sqrt{i\bar{k}/D} = \sqrt{i}\phi_1$.

The selectivity for the DNE reaction defined as the average number of D atoms in the initial hydride product (Kemball, 1954) was shown to be related to the effectiveness factor ratio (Dwyer et al., 1968)

$$M = \text{initial}\left[\sum_{i=1}^{n} i\,a_i \Big/ \sum_{i=1}^{n} a_i\right] = \frac{n\lambda_1^{+}}{\lambda_n^{+}} = \frac{\eta_1}{\eta_n} \tag{6}$$

where n is the number of exchangeable hydrogen sites on the reactant hydride. (For DNE reaction studies, the t-butyl ion is observed rather than the neopentane molecule; therefore $n = 9$.)

Experimental

The method of preparation of nonuniformly active Pt catalysts was described in a previous article (Shyr and Ernst, 1980). The method involved impregnation of γ-alumina particles of spherical geometry with chloroplatinic acid solution containing the coingredients citric acid and NaBr, which modified the Pt profile. The catalyst support was gamma alumina (Rhone Poulenc Inc. Type GOD-30). Properties of the support include: particle dia. 0.36 cm; surface area, 150 m^2/g; total pore volume 1.7 mL/g; and average pore dia., 450Å (45 nm).

A sample of catalyst from the preparation batch was examined by electron probe microanalysis (EPM) and found to have a radial profile of Pt that could be represented by the function $m(1-x)^{\alpha}$ where $\alpha = 1.1 \pm 0.04$ (Hiltzik, 1983).

The batch reaction system was a slightly modified version of an earlier system (Ernst and Wei, 1975). It consisted of a 500 mL spherical Pyrex reactor containing a porous pedestal for

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supporting a catalyst particle and a 1,000 mL spherical Pyrex bulb for premixing D_2 and neopentane. Both vessels were temperature-controlled for isothermal operation and both contained glass-encased magnetic stirrers. The reaction mixture had a D_2-neopentane molar ratio of 1,250:1. Samples were removed batchwise from the reactor at regular time intervals and analyzed on a Kratos model MS 10S mass spectrometer in accordance with procedures described by Sagun and Ernst (1983).

Results and Discussion

Prior to the experimental work, calculations were made to predict how sensitive the model was to catalyst nonuniformity. Figure 1 shows the results of such calculations using Eqs. 5 and 6. At each value of ϕ_1 above about 0.3, the nonuniformity parameter α has a large influence on selectivity. This influence increases with increasing ϕ_1. The symbols in Figure 2 show a_i vs. conversion calculated by Eqs. 1, 4, and 5 for parameter values $\alpha = 1$ and $\phi_1 = 2$. The solid lines represent attempts at fitting these points with the model assuming an incorrect α parameter value (i.e., $\alpha = 0$). The deviation between lines and symbols is qualitative evidence of a poor fit. The fitting procedure involved varying ϕ_1 until minimum ψ was achieved, where

$$\psi = \left\{ \sum_{j=1}^{T} \sum_{i=1}^{n} (a_{i,\text{exp}} - a_{i,\text{calc}})_j^2 / n \cdot T \right\}^{1/2} \tag{7}$$

T is the number of samples taken during a run. The best fit, represented by the lines in Figure 2, occurred at $\phi_1 = 3.7$, where $\psi_{\text{min}} = 0.0090$. This figure illustrates the large deviations which might result between experimental and calculated mole fractions if one attempted to fit the data from a reaction experiment by a model which contained an incorrectly assumed α value.

Preliminary reaction experiments on the catalyst revealed that graphs of ln b_i vs. t or ln b_i vs. ln b_1 yielded straight lines in accordance with Eq. 4. In previous studies (Dwyer et al, 1968; Ernst and Wei, 1975; Sagun and Ernst, 1983) it was shown that at high reaction temperatures the DNE kinetics could not be represented by a single-step exchange process, but rather by a multiple exchange characterized by a desorption parameter β. It was highly desirable in the present study to avoid operating in the multiple exchange region. Adding the parameter β to the

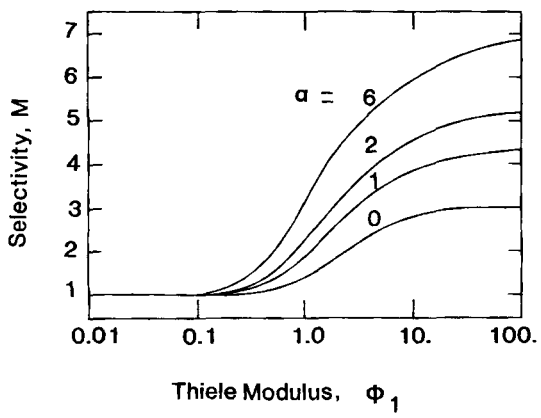

Figure 1. Dependence of the neopentane-deuterium exchange reaction selectivity on the activity profile within a catalyst particle.

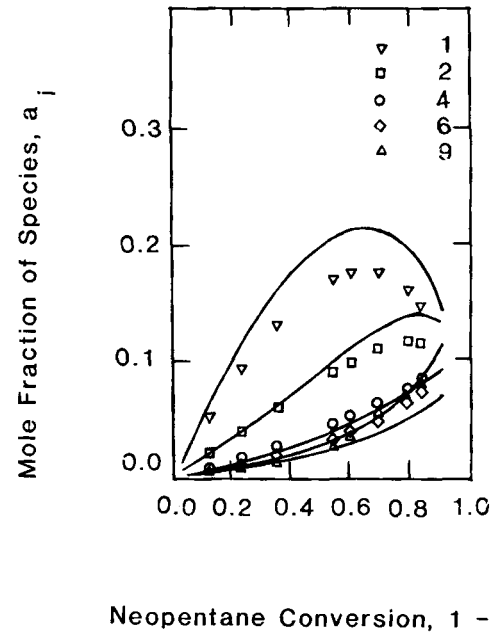

Figure 2. Simulated reaction data for a nonuniformly active catalyst, $\alpha = 1$ (symbols) fitted by a model for a uniformly active catalyst, $\alpha = 0$ (solid lines).

model would make the model less sensitive to the influence of α and hence would make the DNE system less desirable as a probe reaction; however, as shown by Figure 1, in order to maximize the sensitivity of the method it was desirable to maximize ϕ_1. The optimal reaction temperature for the present system was found to be 170°C. Above 170°C, β effects became important, whereas decreasing temperatures below 170°C decreased ϕ_1.

In a previous study on crushed Pt-Al_2O_3 particles (Sagun and Ernst, 1983), β effects were significant even at temperatures lower than 170°C. We are not sure what factor permitted operation at 170°C with negligible β effects in the present study. The method of catalyst preparation may have had an influence on β. In the present study, catalysts were produced by impregnation with a solution containing H_2PtCl_6 and coingredients, whereas in the previous study the catalyst was prepared with a solution of only H_2PtCl_6.

Six reaction runs at 170°C were conducted. Between runs the catalyst was evacuated for 1 h at 1×10^{-7} torr (133×10^{-7} Pa) at reaction temperature. All runs were continued until at least 50% (usually > 90%) conversion of neopentane was achieved. The experimental mole fractions $a_{i,\text{exp}}$ were compared with model calculations $a_{i,\text{calc}}$ for an assumed value of α until the best value of ϕ_1 which produced a minimum ψ value (or ψ_α) was found. This analysis was repeated for a wide range of α values until the lowest value of ψ_α was found. The α value corresponding to the lowest ψ_α value was considered the one which best represented the catalyst. Figure 3 shows a graph of ψ_α vs. α for three of the reaction runs. All three curves pass through a minimum corresponding to a best value of α between 1 and 2. The average best value of α for the six runs was 1.6 ± 0.25 where 0.25 represents the average deviation from the mean. The corresponding average values of ϕ_1 and M for the six runs were respectively 1.03 ± 0.25 and 2.07 ± 0.24.

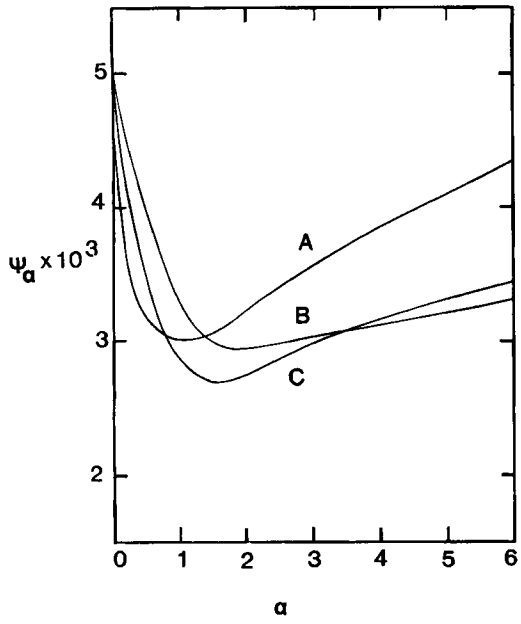

Figure 3. Determination of activity parameter for a catalyst particle by chemical probe method.

ϕ_1 values at minimum ψ_a for the three experiments: A, 1.45; B, 0.72; C, 0.91).

The results of this study are somewhat encouraging in that reasonable agreement was obtained between the α value obtained by the EPM analysis ($\alpha = 1.1$) and by the results of modeling the experimental reaction data ($\alpha = 1.6$). This is not to say that perfect agreement should exist: the EPM analysis measures the distribution of mass of Pt, whereas the reaction study measures the distribution of activity. In theory the two may differ, for example if the average Pt crystallite size varies as a function of radial position within the particle.

The low resolution (lack of sharpness) of the minima in Figure 3 can probably be attributed to the upper limit of operating temperature at which the experiments were constrained. Had it been possible to operate at larger ϕ_1 without imposing β effects the resolution might have been greater. In future studies it might be possible to improve resolution by using catalyst particles that have much smaller average pore sizes than the catalyst used in this study so that large ϕ_1 values can be achieved at lower temperatures.

The method described in this paper may have potential value as a nondestructive chemical probe of catalyst nonuniformity in contrast to EPM. It may have future application as an *in situ* probe in studies in which it is desirable to determine the activity profile of the same particle before and after it has been exposed to deactivating conditions.

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Notation

$\boldsymbol{a}$ = concentration vector for gas phase hydride species with elements a_i, where i refers to the number of D atoms in the species
$\boldsymbol{B}$ = matrix with elements $B(i, i) = (n - i)$ for $i = 0$ to n; $B(i, i-1) = -(n - i + 1)$ for $i = 1$ to n; all other elements = 0
D = catalyst diffusivity
g = constant, $(\alpha + 1)/(\alpha + 2)$
I_p = modified Bessel function of the first kind
$\bar{k}$ = volume average catalytic activity
m = constant = $(\alpha + 1)(\alpha + 2)(\alpha + 3)/6$
p = constant, $1/(\alpha + 2)$
R = particle radius
x = dimensionless distance from center of the catalyst sphere

Greek letters

α = nonuniformity parameter
λ_i = i = element of eigenvalue matrix of $\boldsymbol{B}$ where $\boldsymbol{B} = \boldsymbol{X}\,\Lambda\,\boldsymbol{X}^{-1}$
Λ^+ = diagonal matrix with elements $i\eta_i$

Subscripts and superscript

i = ith species
exp = experimentally determined
calc = calculated
o = initial value

Literature Cited

Dwyer, F. G., et al. "The Kinetics of Deuterium-Neopentane Exchange: Effects of Desorption and Diffusion," *Proc. Roy. Soc.*, **A302,** 253 (1968).

Ernst, W., and D. Daugherty, "A Method for the Study of a Single Spherical Particle with Nonuniform Catalytic Activity," *AIChE J.*, **24** (5), 935 (1978).

Ernst, W., and J. Wei, "Deuterium-Hydride Exchange in a Single Catalyst Particle," *J. Catalysis*, **39,** 303 (1975).

Hiltzik, L. H., "Development of an Experimental Technique for Characterizing the Diffusion-Reaction Behavior of Porous Catalyst Particles," M.S. Thesis, School of Chem. Eng., Georgia Institute of Technology (1983). (The term α in the Results and Discussion section was recalculated to 1.1 using a nonlinear least-squares fit of the equation $f(x) = m(1 - x)^{\alpha}$. The number was previously reported by Shyr, 1980, as 0.9 using a linear least-squares fit of the equation $\ln[f(x)] = \ln(m) + \alpha \ln(1 - x)$.

Kemball, C., "The Exchange Reaction between Neopentane and Deuterium on Evaporated Metallic Films," *Trans. Faraday Soc.*, **50,** 1,344 (1954).

Sagun, G., and W. R. Ernst, "Evaluation of Neopentane-Deuterium Exchange on Pt/Al_2O_3 as a Probe of Physical Phenomena," *J. Catalysis*, **84,** 95 (1983).

Shyr, Y.-S., and W. Ernst, "Preparation of Nonuniformly Active Catalysts," *J. Catalysis*, **63,** 425 (1980).

Wang, J., and A. Varma, "On Shape Normalization for Nonuniformly Active Catalyst Pellets," *Chem. Eng. Sci.*, **35,** 613 (1980).

Wei, J., and C. D. Prater, "The Structure and Analysis of Complex Reaction Systems," in *Adv. Catalysis*, D. D. Eley, P. W. Selwood, and P. B. Weisz, eds., Academic Press, New York, **13,** 203 (1962).

Wei, J., "Intraparticle Diffusion Effects in Complex Systems of First-Order Reactions. I: The Effects in Single Particles," *J. Catalysis*, **1,** 526 (1962a).

———, "Intraparticle Diffusion Effects in Complex Systems of First-Order Reactions. II: The Influence of Diffusion on the Performance of Chemical Reactors," ibid., 538 (1962b).

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