Simultaneous Diffusion, Adsorption, and Reaction in Fluid Catalytic Cracking Catalysts

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Simultaneous diffusion, adsorption, and reaction that take place inside the zeolitic component of equilibrium commercial fluid catalytic cracking (FCC) catalysts were described by means of heterogeneous models. *n*-Hexadecane was used as a test reactant at high temperatures (440−550 °C) over two different equilibrium catalysts under very short contact times up to 10 s in a Riser Simulator reactor. The system's parameters were obtained by fitting the model to the reactant's gas-phase concentration versus reaction time data. When zeolite intracrystalline diffusion was first assumed as the controlling mechanism for mass transfer, its energy of activation resulted close to the heat of adsorption, suggesting that diffusion in the zeolite micropores could be indeed controlling. The solution under this new approach led to the obtention of parameters that were consistent with the existence of strong diffusion limitations for the reaction and with lower activity in the low unit cell size catalyst. Diffusion, which would be a nonactivated process, had coefficients that were essentially the same in both catalysts, while the energies of activation of the reaction were different and reflected the higher relative importance of the mechanism of monomolecular cracking in the more dealuminated catalyst. The need for a careful assessment of adsorption parameters in FCC catalysts was confirmed by the fact that their magnitudes change significantly as a function of temperature, with adsorption being somewhat stronger on the higher unit cell size catalyst in the temperature range of interest for FCC. The method employed proved to be adequate and sensitive for the quantification of these issues, which are important in reactor design and simulation and catalyst evaluation procedures.

Introduction

The fluid catalytic cracking (FCC) of hydrocarbons is a central process in the refineries, because it is not only a major fuel producer (e.g., gasoline and diesel fuel) but also a supplier of raw materials such as light olefins, isobutylene, isobutane, etc., for a number of petrochemical and associated processes.[1] The cyclic process is conducted between a transport, diluted fluidized-bed reactor—the riser reactor—where the very short contact time between catalyst particles and reactant hydrocarbons deactivates the catalyst by coke deposition. A stripping step is performed after the reaction by means of steam injected in order to remove hydrocarbons that are adsorbed on the catalyst surface, and then catalyst particles pass through a dense fluidized bed—the regenerator—where coke is burnt off. Finally the regenerated catalyst, carrying the heat from coke combustion that is necessary to maintain endothermic cracking reactions, is sent back to the reactor to face again the hydrocarbon feedstock.[2]

In the modeling of the FCC process, cracking reaction kinetics is usually described by pseudohomogeneous, lumped,[3−5] or empirical models.[6,7] This is an important limitation when modeling this complex system, where kinetics, adsorption phenomena, and hydrodynamics have to be considered. Moreover, most of the simulation models for the various types of FCC units do not take adsorption into account, thus neglecting an issue that may have a significant impact on reactor simulation, particularly on the hydrodynamics.[8]

So far, only a few studies were devoted to hydrocarbon adsorption in the FCC process. Hershkowitz and Madiara[9] used a pulsed microbalance to estimate simultaneous adsorption and coking by *n*-decane on FCC catalysts. Farag et al.[10] assessed adsorption constants with a four-lump model on data obtained with an unsteady-state pulse technique. Pruski et al.[8] followed an interesting approach to show that it was possible to estimate phase distribution coefficients in a Riser Simulator reactor without simultaneously considering reaction kinetics. Sowerby and Becker[11] estimated adsorption equilibrium constants using an integrated form of van't Hoff's equation that, after some assumptions, required knowledge of the heat of condensation, the entropy of adsorption, and the proton affinities of the adsorbate and the catalyst. These previous works confirmed that it is necessary to address more soundly the evaluation of adsorption parameters under actual reaction conditions. Moreover, the interrelationship between the processes of diffusion, adsorption, and reaction in the catalyst particles is an even more complex problem, and to describe this catalytic system, theoretical models needed to make use of severe restrictions and assumptions, like steady state (e.g., ref 12).

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Table 1. Catalyst Properties

catalyst	surface area ($m^2\ g^{-1}$)	zeolite content (%)	unit cell size (Å)	rare-earth oxides (%)
E	147	11.5	24.29	1.42
O	151	15.9	24.24	0.00

The existence of diffusion limitations when cracking large molecules of vacuum gas oils is ordinarily accepted (e.g., refs 13 and 14), but there exists the need of direct measurements to elucidate the true role of zeolite micropore diffusion.[14]

Another fact strongly linked to these issues is the difficulty to reproduce the FCC process conditions in the laboratory. In fact, most of the related work has been performed on fixed-bed reactors, besides the many inherent problems in relation to FCC that are associated with the design and operation of these types of reactors.[1,15] The Riser Simulator reactor[16] is a laboratory unit that has been specifically designed to overcome these problems, because it closely mimics the actual FCC conditions, and that has proven its versatility, being used in studies devoted to kinetic modeling,[17] catalyst evaluation,[18] fundamental aspects,[19] and novel operative approaches.[20]

It is the objective of this study to analyze the simultaneous effects of diffusion, adsorption, and reaction at a high temperature inside the particles of commercial FCC catalysts and to establish quantitatively their relative importances, by means of experiments with two equilibrium catalysts and *n*-hexadecane as a test reactant in a Riser Simulator reactor.

Experimental Section

Two commercial FCC catalysts obtained from running refineries were used: equilibrium catalysts E (PRE-50AR, Engelhard) and O (Octavision, FCC S.A., Brazil). Their properties are presented in Table 1. The average particle size in both catalysts is 70−100 μm. Zeolite unit cell sizes were determined by means of the ASTM D-3942-85 technique, and the zeolite content and catalyst physical properties were assessed by conventional nitrogen adsorption at 77 K. The reactant was *n*-hexadecane (Fluka, 99.9% minimum) without further treatment.

All of the experiments were performed in a batch, fluidized-bed, stirred tank reactor, the Riser Simulator[16] that has been described thoroughly elsewhere.[8,15,21] It is to be mentioned that, because of very intense mixing in the unit, external (fluid-phase) temperature and concentration gradients are excluded.[21] The experimental conditions were the following: temperatures of catalyst E, 475, 500, and 550 °C; temperatures of catalyst O, 440, 500, and 550 °C; mass catalyst-to-reactant ratio, 5.15; mass of catalyst, 0.8 g; reaction times, from 0.5 to 10 s. After reaching the target experimental conditions, the following steps were performed: injection of the reactant with instantaneous vaporization, previous filling of the reactor with inert nitrogen at atmospheric pressure, reaction during a given contact time, evacuation of the reactor's gas phase, which is essentially instantaneous, and analysis by on-line capillary gas chromatography.

Theoretical Model and Numerical Analysis Procedure

The particles of the commercial catalysts used were composed of a certain amount of Y zeolite deposited on a matrix, catalyst E having rare earths that are usually added to increase zeolite structural stability and acidity. Y zeolite has a tridimensional channel system with pore openings of 7.4 Å diameter that link cavities (supercages) of about 13 Å diameter.[22]

Most important assumptions in the model to describe diffusion, adsorption, and reaction are as follows:

(1) Restrictions to mass transfer, adsorption, and reaction in the matrix component are considered negligible, as compared to those in the zeolite.[23,24]

(2) The reactor design and operation ensure complete mixing in the gas phase; then, no concentration and temperature gradients are observed outside the catalyst particles.[21]

(3) Zeolite intracrystalline diffusion was assumed to be the controlling mechanism for mass transfer in the catalyst particles. The application of a Fick's law type expression, with constant diffusion coefficients, was admitted,[25] with no distinctions being made between diffusing and adsorbed phases. The diffusion process is assumed to have an exponential dependence with temperature and, to reduce the number of parameters to be assessed, the diffusivities were assumed to be the same in both catalysts, because of the fact that the pore systems of the zeolites are identical.

(4) Adsorption equilibrium is attained at the zeolite crystal surface, with the isotherm being linear ($q = KC$, where K is the Henry's constant). The temperature dependence was described by the van't Hoff equation.

(5) *n*-Hexadecane has been used successfully as a test reactant for FCC-related studies.[26,27] The cracking reaction is considered to be of first order in the concentration of reactant *n*-hexadecane, to follow Arrhenius' law, and because of low conversion, deactivation is not taken into account.

(6) The particles are considered spherical and isothermal.

The following dimensionless variables are defined, with effective parameters being discussed below in the text,

$$\tau = \frac{D_{\mathrm{eff}}}{{r_{\mathrm{c}}}^2}t, \quad \rho = \frac{r}{r_{\mathrm{c}}}, \quad \xi = \frac{q(r,t)}{K_{\mathrm{eff}}C_0}, \quad \chi = \frac{C(t)}{C_0} \tag{1}$$

that allow the mass balance for the reactant inside the zeolite pores to be written as

$$\frac{\partial \xi}{\partial \tau} = \nabla^2 \xi - \phi^2 \xi \tag{2}$$

where

$$\phi = r_{\mathrm{c}}\sqrt{k_{\mathrm{eff}}/D_{\mathrm{eff}}} \tag{3}$$

is the Thiele modulus.

The equation is subjected to the following initial and boundary conditions:

$$\xi(\rho,0) = 0 \tag{4}$$

$$\left.\frac{\partial \xi}{\partial \rho}\right|_{\rho=0} = 0 \tag{5}$$

$$\xi(1,\tau) = \chi(\tau) \tag{6}$$

To solve the above system, the linear driving force (LDF) concept for diffusion, adsorption, and reaction in porous catalysts can be used. With the previous definition of the volume-averaged concentrations, the formula developed by Kim[28] was used in order to transform the partial differential equation (2) into an ordinary differential equation. The system can now be described by

$$\frac{d\bar{\xi}}{d\tau} = \frac{s_1}{s_2}(s_1\chi - \bar{\xi}) \qquad (7)$$

subjected to the initial condition

$$\bar{\xi}(0) = 0 \qquad (8)$$

and where

$$\bar{\xi} = 3\int_0^1 \xi\rho^2 \, d\rho \qquad (9)$$

$$s_i = \sum_{n=1}^{\infty}[6/(\phi^2 + n^2\pi^2)^i] \qquad (10)$$

This mass balance in the catalyst particles can be linked to the mass balance in the reactor's gas phase (because reactor evacuation is instantaneous, its dynamics is not included):

$$\frac{d\chi}{d\tau} = -\alpha\left(\frac{d\bar{\xi}}{d\tau} + \phi^2\bar{\xi}\right) \qquad (11)$$

where

$$\alpha = \frac{V_s}{V_g}K_{eff} \qquad (12)$$

which is subjected to the initial condition

$$\chi(0) = 1 \qquad (13)$$

It can be easily shown that the system of ordinary differential equations (7) and (11) can be solved by applying the Laplace transform to yield

$$\chi(s) = \frac{(s_2/s_1)s + 1}{(s_2/s_1)s^2 + (1 + \alpha s_1)s + \alpha s_1\phi^2} \qquad (14)$$

Finally, the time response for the concentration of *n*-hexadecane in the reactor's gas phase is

$$C(t) = C_0\left[\frac{\psi^{-1} - a}{b - a}\exp(-at) + \frac{b - \psi^{-1}}{b - a}\exp(-bt)\right] \qquad (15)$$

where

$$\psi = \left(\frac{D_{eff}}{r_c^{\,2}}\frac{s_1}{s_2}\right)^{-1} \qquad (16)$$

and *a* and *b* are complex functions of the diffusion, adsorption, and kinetics parameters:

$$a = \frac{\beta - \delta}{2} \qquad (17)$$

$$b = \frac{\beta + \delta}{2} \qquad (18)$$

where

$$\beta = \left(1 + \frac{V_s}{V_g}s_1K_{eff}\right)\psi^{-1} \qquad (19)$$

and

$$\delta = \left(\beta^2 - 4\frac{V_s}{V_g}\frac{D_{eff}}{r_c^{\,2}}K_{eff}k_{eff}\frac{s_1^{\,2}}{s_2}\right)^{1/2} \qquad (20)$$

A modified Levenberg–Marquardt method to solve nonlinear least-squares problems[29] was used to assess the diffusive, adsorptive, and kinetic parameters simultaneously. To diminish parameter correlation, preexponential factors and energies of activation were assessed by fitting the predictions of the model for the reactant's fractional concentration C/C_0 in the gas phase (eq 15) to the experimental values observed in the whole set of experiments for each catalyst (various reaction times at different thermal levels). Initial guesses for E_d in this procedure were taken from a wide range of reported values.[25] The values for the various parameters other than diffusive, adsorptive, and kinetic that are involved in eq 15 are presented in Table 2. It is to be noted that the parametric sensitivity of the system was analyzed previously and proved to be adequate.

Results and Discussion

The optimum values of the effective diffusive, adsorptive, and kinetic parameters (see below in the text), and its spans resulting from fitting of the model to the experimental values, are presented in Table 3 for each of the catalysts. In general terms, the spans given by the 95% confidence intervals and the cross-correlation matrices of these optimizations can be considered acceptable. Particularly, the spans of the activation terms are smaller than those of the preexponential terms.

The value of the diffusion coefficient D_{eff} that can be calculated for this system (around 1×10^{-11} cm^2 s^{-1}) is comparable to those obtained on stirred tanks by Ma and Lee[30] for X zeolites, although the energy of activation (14.1 kcal mol^{-1}) is higher and similar to the one for diffusion of *n*-butane on NaY[31] (14.3 kcal mol^{-1}). It is interesting to observe that this energy of activation is similar to the heat of adsorption (average, 15.7 kcal mol^{-1}). In that sense, it has been pointed out[25,32] that high values of energies of activation that were reported in works carried out with pelletized zeolites at low temperatures could be explained as an indication that the mass-transfer processes could have been controlled, indeed, by the macropore diffusion and not by the intracrystalline diffusion. The small particle size used in this work excludes that possibility. Nevertheless, under an analogous reasoning, it is now possible to consider an alternative model in which mass transfer is controlled by the zeolite micropore diffusion. In effect, in that case, the corresponding mass balance in the zeolite component of the catalysts should be written as

$$\epsilon_i\frac{\partial C_i}{\partial t} = \epsilon_i D_i\nabla^2 C_i - (1 - \epsilon_i)K\frac{\partial C_i}{\partial t} - (1 - \epsilon_i)kKC_i \qquad (21)$$

where ϵ_i is the zeolite void fraction.

When dimensionless variables are used, this equation can be transformed easily into eq 2 if the diffusion, adsorption, and kinetic parameters in eqs 3 and 12 are

Table 2. Values of the Parameters in Equation 15

parameter	value
m_c (g)	0.8
r_c (μm)	1
V_g (cm^3)	45
V_s (cm^3)	0.061 (catalyst E) 0.085 (catalyst O)

Table 3. Values of the Preexponential and Exponential Terms for the Effective Diffusion, Adsorption, and Kinetics Parameters, Assessed from the Zeolite Intracrystalline Diffusion Model, Eq 2, with 95% Confidence Intervals

parameter	catalyst O	catalyst E
k_0 (s^{-1})	$1 \times 10^{13} \pm 7.80 \times 10^{12}$	$(3.37 \pm 4.46) \times 10^{9}$
E_a (kcal mol^{-1})	49.83 ± 2.10	35.99 ± 2.70
K_0	$(5.82 \pm 3.32) \times 10^{-2}$	$(7.48 \pm 4.73) \times 10^{-2}$
ΔH_{ads} (kcal mol^{-1})	15.78 ± 1.53	15.66 ± 1.83
D_0 (cm^2 s^{-1})	$(9.5 \pm 3.6) \times 10^{-8}$	$(9.5 \pm 3.6) \times 10^{-8}$
E_d (kcal mol^{-1})	14.11 ± 1.25	14.11 ± 1.25

Table 4. Diffusion, Adsorption, and Reaction Parameters and the Thiele Modulus at Various Temperatures Evaluated from the Zeolite Micropore Diffusion Model (Eq 21), Calculated Assuming $\epsilon_i = 0.5$[22]

	T (°C)					
	catalyst E			catalyst O		
parameter	475	500	550	440	500	550
$1 \times 10^8 D_i$ (cm^2 s^{-1})	1.499	1.495	1.491	1.311	1.291	1.282
k (s^{-1})	0.103	0.225	0.935	0.005	0.082	0.586
K	1969	1447	829	2736	1250	713
ϕ	11.6	14.8	22.8	3.3	8.9	18.0

replaced by the following definitions:

$$D_{\text{eff}} = \frac{D_i}{1 + \left(\frac{1-\epsilon_i}{\epsilon_i}\right)K} \tag{22}$$

$$K_{eff} = \epsilon_i\left[1 + \left(\frac{1-\epsilon_i}{\epsilon_i}\right)K\right] \tag{23}$$

$$k_{\text{eff}} = \frac{\left(\frac{1-\epsilon_i}{\epsilon_i}\right)K}{1 + \left(\frac{1-\epsilon_i}{\epsilon_i}\right)K}\,k \tag{24}$$

Therefore, the solutions of eqs 2 and 21 are identical provided that these redefinitions are produced. Then, as a consequence, the parameters assessed from eq 2 should be considered "effective". By inspecting eq 22 and considering typical values for the void fraction ϵ_i in Y zeolite to be around 0.5[22] and the regressed values of K_{eff}, the effective diffusion coefficient D_{eff} would be very close to D_i/K. Consequently, it can be understood that the temperature dependence of the diffusion process, as it was modeled, could indeed be essentially the one of the adsorption process, that is, the heat of adsorption. Indeed, when D_i is evaluated as the product between D_{eff} and K, it is almost independent of the temperature for both catalysts. Diffusion for n-hexadecane inside the zeolite pores of an equilibrium FCC catalyst, then, would not be a strongly activated process. The values of the parameters from this micropore diffusion model and the Thiele modulus are presented in Table 4, calculated from those in Table 3 and the definitions in eqs 22−24. The predictions of the model for the values of the fractional reactant concentration in the reactor's gas phase as a function of residence time, at the various temperatures, are presented in Figures1 and 2, where it can be seen that a close simulation is achieved for each of the catalysts.

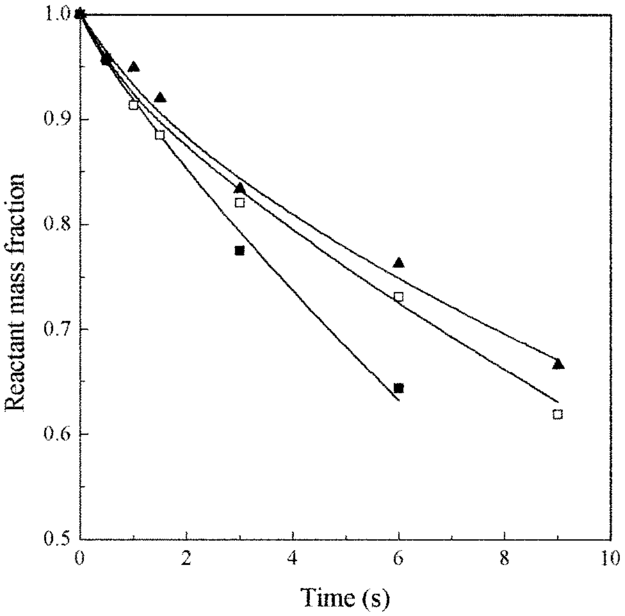

Figure 1. Mass fractional concentration of n-hexadecane as a function of reaction time. Catalyst E. Symbols: (▲) 475 °C; (□) 500 °C; (■) 550 °C. Line: model's response.

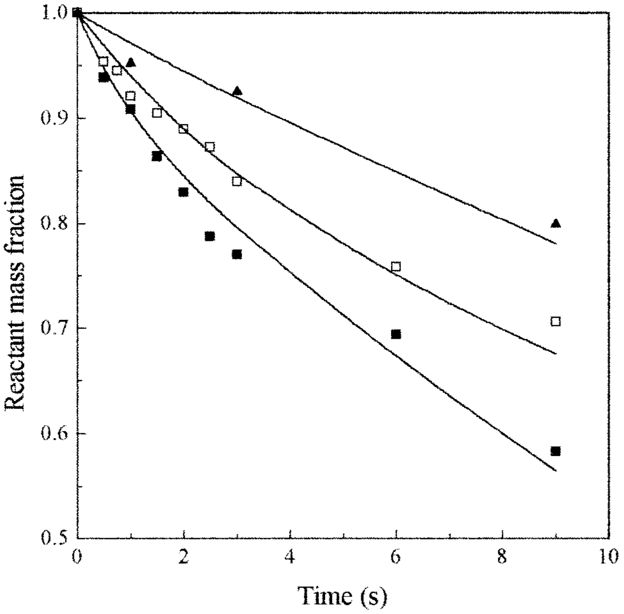

Figure 2. Mass fractional concentration of n-hexadecane as a function of reaction time. Catalyst O. Symbols: (▲) 440 °C; (□) 500 °C; (■) 550 °C. Line: model's response.

It can be seen that the Thiele modulus, typically larger than 8, is quite large under all conditions for both catalysts. This is not unexpected, because activity is large, and diffusion restricted, in the zeolite pores. Moreover, if a new regression is performed without imposing equal diffusivities in both catalysts, it yields diffusion coefficients that are very similar, thus confirming that the previous assumption of equal diffusion processes was indeed a good one.

The relationships between the diffusion process and the cracking reaction kinetics clearly show that there are strong diffusion limitations for the chemical reaction in this system. It had been claimed that direct measurements to address the role of micropore diffusion were missing.[14] The activity of catalyst E, as expressed by the kinetic coefficient k (refer to Table 4), is larger than that of catalyst O at the various temperatures used (e.g., 0.225 and 0.082 s^{-1} at 500 °C, respectively). It has to be considered that the degree of dealumination is higher in catalyst O, which means that the number of acid sites, that are associated with the number of aluminum atoms present in the zeolite, is consequently smaller, in turn resulting in lower activity on a volume basis. The acidity in catalyst E is also increased by the rare-earth elements present. The values of the kinetic constants of these commercial catalysts are in line with the fact that they possess different zeolite loadings (higher on catalyst O), a common practice in FCC catalyst technology, so as to compensate for differences in activities.

The numbers of predicted aluminum atoms per unit cell size −5.6 and 11.4, for catalysts O and E, respectively, according to the Breck's correlation,[22] confirm the higher dealumination of catalyst O, which is also consistent with the lack of stabilizing rare earths. However, the influence of the fact that the acid sites in catalyst O are more isolated and, consequently, expected to be stronger than those in catalyst E,[33] is reflected in the values of the energy of activation E_a. In effect, the value of this parameter in catalyst O is larger. It has been shown that the product distributions in the cracking of paraffinic compounds on zeolitic catalysts, as a result of the relationship between the cracking mechanisms (monomolecular cracking via pentacoordinated carbonium ions, and conventional β-scission cracking via tricoordinated carbenium ions), change as a function of temperature to show that monomolecular cracking has a higher energy of activation than β-scission cracking.[34,35] On the other hand, de la Puente and Sedran[19] showed that this relationship between cracking mechanisms is also a function of the degree of catalysts dealumination in FCC catalysts containing Y zeolite: the more dealuminated the catalyst, the more prevalent the monomolecular process, because of the higher localized disturbing influence of field gradients in zeolite pores on the reacting molecules, as a consequence of increased site isolation. This effect is even more important on catalysts equilibrated in commercial processes, because dealumination through the zeolite crystals is more homogeneous than, for example, that resulting from dealumination by steam at high temperatures in the laboratories.[19] Then, the larger overall energy of activation of the reaction observed in catalyst O (refer to Table 3) is a consequence of the higher relative incidence of monomolecular cracking, and it is consistent with catalyst properties and prevailing reaction mechanisms.

The value of the preexponential adsorption parameter K_0 is somewhat higher in catalyst E, while ΔH_{ads} is the same in both catalysts (refer to Table 3). As a consequence, the dimensionless adsorption constant K is higher in catalyst E at all of the thermal levels, a fact that could be associated with a higher number of adsorption sites in catalyst E, probably linkable to the number of acid sites.

It is not simple to compare these values of adsorption parameters in FCC catalysts with the few ones previously reported in the literature, mainly because they were obtained following very different procedures and approaches. However, some points are comparable. For example, Pruski et al.[8] evaluated phase distribution coefficients that, for the case of light cycle oil, a hydrocarbon lump whose average molecular weight is typically very close to that of n-hexadecane, indicated a heat of adsorption ΔH_{ads} of approximately 16.1 kcal mol^{-1}, which is very close to the average value of 15.7 kcal mol^{-1} of this work. Moreover, this value is included in the wide range of reported heats of sorption of organic molecules on zeolite sites that extends from 10 to 30 kcal mol^{-1}.[36] Concerning Henry's constants K, they can be compared with the coefficients assessed by Pruski et al.[8] by considering the amount of zeolite on the catalyst and its density; although the catalyst they used was not fully characterized, the coefficients are very similar (for example, at 550 °C, average 66 $cm^3\ g^{-1}$ for n-hexadecane on catalysts E and O, against values of about 60 $cm^3\ g^{-1}$ for light cycle oil in ref 8). Herskowitz and Madiara[9] determined that Henry's constant for decane at 300 °C is approximately 470.

Conclusions

Simultaneous diffusion, adsorption, and reaction at high temperature in equilibrium commercial FCC catalysts can be described with a more fundamental approach by means of heterogeneous models. The corresponding parameters can be evaluated by fitting the model to short contact time conversion data gathered in a Riser Simulator reactor. A model considering zeolite micropore diffusion as the controlling mechanism for mass transfer was finally adopted, and resulting system parameters were consistent with the following facts: (a) strong diffusion limitations to the cracking reaction under actual FCC conditions, with diffusion being a nonactivated process; (b) lower reactivity, because of less active sites, and higher energy of activation, because of the higher importance of monomolecular cracking in more dealuminated, lower unit cell size catalysts; (c) somewhat stronger hydrocarbon adsorption in higher unit cell size catalysts in the temperature range of interest for FCC. These facts stress that it is necessary to evaluate these parameters, that are needed in reactor design and simulation and catalyst evaluation, very carefully. This approach proved to be sensitive and adequate.

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Nomenclature

a, b = parameters defined in eqs 17 and 18, s^{-1}
C = reactant concentration in the gas phase, mol cm^{-3}
D = diffusion coefficient, $cm^2\ s^{-1}$
ΔH_{ads} = heat of adsorption, kcal mol^{-1}
E_a = energy of activation of the cracking reaction, kcal mol^{-1}
E_d = energy of activation of the diffusion process, kcal mol^{-1}
k = kinetic constant, s^{-1}
K = Henry's constant ($K = q/C$)
m_c = mass of catalyst, g

q = concentration of the adsorbed reactant, mol cm^{-3}
r = radial coordinate in the zeolite crystals, cm
r_c = radius of the zeolite crystals, cm
R = universal gas constant, kcal K mol^{-1}
s = Laplace transform parameter
s_1, s_2 = coefficients defined in eq 10
t = time, s
V_g = volume of the gas phase, cm^3
V_s = volume of the zeolite phase, cm^3

Greek Letters

α = parameter defined in eq 12
β, δ = parameters defined in eqs 19 and 20, s^{-1}
ϵ_i = zeolite void fraction
χ = dimensionless reactant concentration in the gas phase
ρ = dimensionless radial coordinate
ξ = dimensionless concentration of the adsorbed reactant
τ = dimensionless time
ϕ = Thiele modulus, defined in eq 3
ψ = parameter defined in eq 16, s

Subscripts

0 = preexponential parameters
i = in reference to the zeolite micropore diffusion model
eff = effective parameters

Superscript

- = volume-averaged variables

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