Adsorption of Hydrocarbons on FCC Catalysts under Reaction Conditions

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A modified CREC Riser Simulator reactor was used in order to assess the adsorption constants of various hydrocarbons produced in the cracking of *n*-hexadecane over an equilibrium commercial FCC catalyst at 550 °C. Complementary experiments were performed with *n*-hexane on both the same catalyst and a pure HY zeolite. A method to estimate apparent hydrocarbon adsorption constants, based on mass balances, the assumption of Henry's law-type behavior, and the compositions observed in two samples, was proposed. One sample was collected immediately after reaction, representing the gas phase that is in equilibrium with the catalysts, and the other one included adsorbed hydrocarbons. It was shown that when a mixture of hydrocarbons produced by cracking reactions contacts the catalysts, there exists a selective enhancement in the adsorption of those hydrocarbons that individually adsorb more strongly. Additional experiments with simple mixtures and no chemical reaction confirmed these observations. Evidence suggests that the diffusive mass transport process in the catalyst particles plays an important role.

Introduction

One of the central aspects of catalysis is the adsorption of the reactants on the active sites of the catalyst. In most of the commercial applications of micro- and mesoporous solid catalysts, mass-transfer limitations are very important, and the accessibility to the active sites has an important effect on the observed activity of a catalyst.[1] The development of new catalyst formulations for the oil refining industry demands the prediction of the performance of commercial catalysts; that is usually accomplished with the help of pilot plant and/ or laboratory facilities.[2−3] This is particularly true for the process of catalytic cracking of hydrocarbons (FCC), where the impact of the catalyst on the overall performance of the commercial unit justifies continuous efforts to guarantee the use of the best available formulation.

FCC is one of the key processes in the petroleum industry, aimed at the conversion of heavy feedstocks into lighter, more valuable products such as liquefied petroleum gases (LPG), gasoline, and diesel fuel. It has been shown that adsorption phenomena in the riser reactor strongly influence the overall reactor hydrodynamics and reaction kinetics.[4] Before regeneration in the cyclic process, the FCC catalyst particles pass through the stripper vessel, where steam is injected in order to remove entrained and adsorbed hydrocarbons from the spent catalyst. This is accomplished in a dense phase fluidized bed where the catalyst or emulsion phase is circulated in countercurrent flow to the steam. In the stripper, about 5−30 wt % of the chemical species that adsorb on the catalyst surface corresponds to hydrocarbons that can be recovered.[5] The amount of adsorbed hydrocarbons depends mainly on the properties of the cracked feedstock, the characteristics of the catalyst, and the design and operating conditions of the hardware. Strippable hydrocarbons not desorbed in the stripping step are directed to the regenerator, where they are burnt. The higher the hydrogen/carbon ratio in the hydrocarbon mixture carried to the regenerator, the higher the regeneration temperatures; in turn, this produces catalyst irreversible deactivation and, more adversely, limits catalyst circulation rate, resulting in losses of conversion and valuable product yields. Therefore, poor stripping results in significant losses in the overall FCC unit profitability.

One important parameter that is frequently disregarded in the protocols of evaluation of commercial FCC catalysts is the one concerning adsorption (either true constants or approximate coefficients). This information could assist in modeling and simulation of catalytic cracking units, where a sound knowledge of diffusion, adsorption, kinetics, and hydrodynamics issues is necessary.[6] Moreover, the knowledge of adsorption processes and the parameters controlling them is indispensable concerning design and simulation of the stripping step. Indeed, laboratory devices such as the fixed bed microactivity (MAT) reactors, fixed fluidized bed reactors, or even some pilot units do not permit us to measure properly the extension of hydrocarbon adsorption. Indeed, when pseudohomogeneous models are used, the adsorption parameters actually combine adsorption, diffusion, and mass-transfer effects.[7] The problem is even more severe under the conditions of the commercial FCC operation, because data and conclusions are masked

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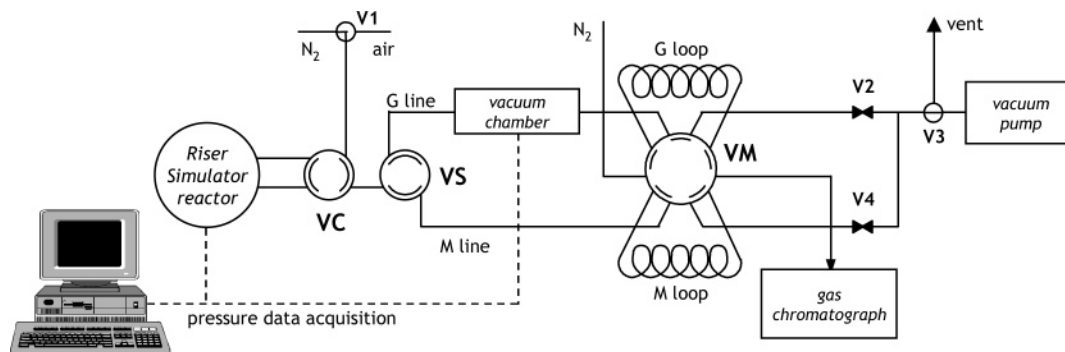§ Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello.

Figure 1. CREC Riser Simulator. Setup configuration.

by the simultaneous existence of the various transport and chemical processes in an extraordinary complex system.

Among the laboratory devices used to assess adsorption constants, an oscillating microbalance was used by Zhu et al.[8] with light alkanes over silicalite at temperatures under 200 °C. A similar device was used by Hershkowitz and Madiara[9] with decane over LaY zeolite at temperatures under 300 °C. Also Lee et al.[10] contacted various paraffinic and aromatic hydrocarbons with commercial FCC catalysts under nonreacting conditions in a microbalance. In a very different approach, a kinetic model was applied to the conversion of vacuum gas oil in a fixed bed reactor operated with pulses of reactant that allowed the simultaneous assessment of adsorption and kinetics parameters.[11] De Lasa and co-workers studied the adsorption of hydrocarbons on FCC catalysts using the CREC Riser Simulator, a batch, fluidized bed laboratory reactor;[12] e.g., Pruski et al.[13] and Atias et al.,[14] focused on the simultaneous adsorption and reaction phenomena.

In this work, the CREC Riser Simulator reactor was modified in order to assess the adsorption constants of hydrocarbons on FCC catalysts, assuming the idea by Martignoni that the differences between the composition of a sample of the gas phase in equilibrium with the catalysts and the composition of a sample including desorbed hydrocarbons, both at a given contact time, would produce the necessary information.[15] It is the objective of this paper to define a proper method to estimate apparent hydrocarbon adsorption constants on commercial FCC catalysts under reaction conditions.

Experimental Section

The CREC Riser Simulator[12] was designed specifically for FCC-related studies. The basic design concept of the unit considers that a small slice of an ideal riser reactor, comprising the mixture of catalyst particles and hydrocarbons that "see" each other while moving along the riser after being put into contact, can be located in a batch reactor with internal recirculation. Thus, the residence time and position along the riser are equivalent to the reaction or contact time in the Riser Simulator. An impeller rotating at very high speed (7500 rpm) on top of the chamber that keeps the catalyst between two metal porous plates induces the internal circulation of the reacting mixture in an upward direction through the chamber, thus fluidizing the catalyst. In the original design, when the reactor is at the desired experimental conditions, the reactant is fed through an injection port, and immediately after the reaction time is attained, products are evacuated instantly by opening automati-

cally the reactor to a large, hot vacuum chamber. After that, a sampling valve is actuated to get a sample from the vacuum chamber, which is analyzed by gas chromatography. Standard configurations of this setup can be observed in, for example, Tonetto et al.[16]

This conventional configuration was not modified structurally, but some new auxiliary parts were added and the operative mode was changed for this work, the present setup arrangement being shown in Figure 1.[17] Part of the changes was the addition of a three-way selecting valve VS and a 10-port valve VM with two sampling loops. The selecting valve VS directs the gases being extracted from the reactor to either the vacuum chamber or the loop M, where high vacuum also exists. Sample M, which is taken at the preset reaction time during a very short time period, is very small and represents the gas phase that is in equilibrium with the catalyst at that moment. After that, the selecting valve VS diverts the flow from the reactor to the vacuum chamber; this mixture contains not only the gas phase from the reactor but also a fraction of the hydrocarbons that were adsorbed on the catalyst surface. Once a preset value of pressure is reached in the reactor, the closing valve VC acts and ends the extraction step. The loop G can be filled later, sampling from the vacuum chamber. All the valves are actuated automatically with high-speed devices. The evolution of the pressure in the reactor and vacuum chamber is recorded by high-accuracy digital sensors.

The catalytic tests were performed using n-hexadecane as a model compound and both pure HY zeolite catalyst (specific surface area, 660 m^2/g; Si/Al ratio, 2.7) and an equilibrium FCC catalyst (E-cat) taken from a running refinery (specific surface area, 125 m^2/g; micropore volume, 0.043 cm^3/g; rare earth content, 2.94%; Ni, 5066 ppm; V, 5845 ppm; Fe, 4200 ppm; MAT activity, 63%). The testing conditions were the following: catalyst-to-oil ratio (CTO) of 7.50 and 1.15, injected reactant volume of 0.17 mL, reaction temperature of 550 °C, and reaction times of 6, 8, and 10 s. Additional experiments were done using n-hexane on the E-cat at 250 and 550 °C, (CTO 7.50, injected volume 0.2 mL), and zeolite HY at 550 °C (CTO 1.38, injected volume 0.2 mL). The difference in the values was an attempt to approximate the contact with the zeolite in the E-cat (zeolite mass-to-reactant ratio). Both samples M and G were analyzed by standard capillary gas chromatography on an HP6890Plus gas chromatograph with a cross-linked methyl silicone column. Coke yields were determined by means of a temperature-programmed oxidation and further methanation procedure.[18] Conversion was defined from sample G as 100 − reactant concentration
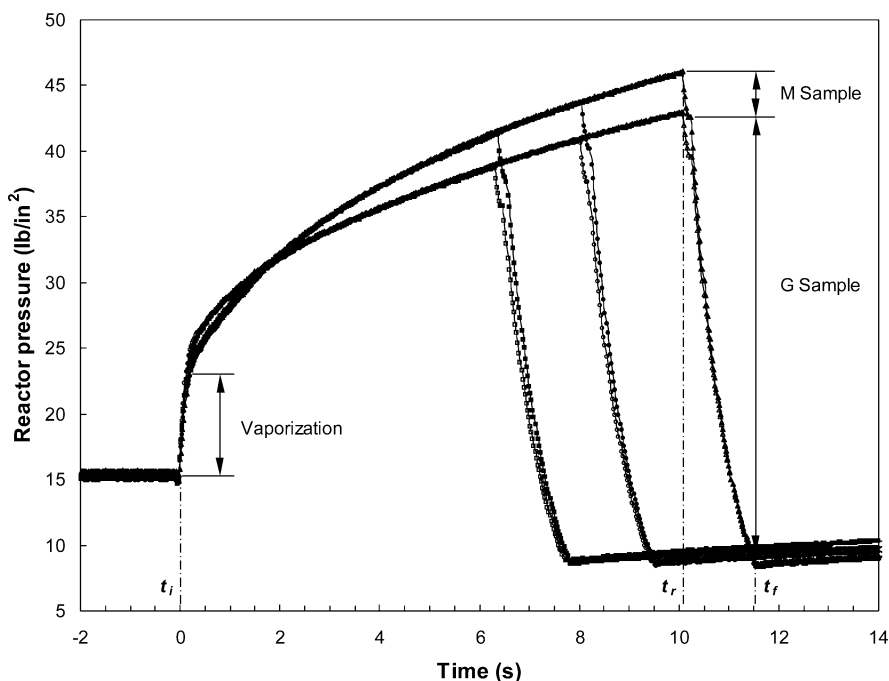
Figure 2. Pressure profiles for experiments with *n*-hexadecane on E-cat. Temperature 550 °C and (■) 6-, (●) 8-, and (▲) 10-s reaction time. Symbols: closed, CTO 7.5; open CTO 1.15.

− coke yield. Mass balances for each experiment were performed based on the experimental information (volume, temperature, pressure, mean molecular weight) in the different sectors of the unit, the differences between injected and recovered hydrocarbon masses being less than ±7% in all the tests.

Results and Discussion

The evolution of the pressure in the reactor plays an important role in the method proposed. In the experiments with *n*-hexadecane, the various experimental steps can be observed by the pressure evolution in the reactor (see Figure 2). Vaporization jumps are very sharp, and then the increase in pressure due to the cracking reactions is observed until the preset reaction time is attained. In that moment, the reactor is opened and the collection of sample M is performed during a short time (note the small decrease in pressure). Then the almost complete evacuation of the reactor, which is very fast, is accomplished. The pressures observed during vaporization for the experiments at CTO 1.15 are higher than those attained at CTO 7.50, which is consistent with the fact that less catalyst is used in the first case, resulting in less reactant adsorption. For a given CTO and set of reaction conditions, the pressure profiles overlap each other under exactly the same evolution, thus indicating that a very similar chemical reaction path was followed. The slope of the pressure profiles during the reaction segment for CTO 7.50 is steeper than that for CTO 1.15, thus denoting faster chemical reaction rates associated with the higher catalyst masses used. Finally, the total increase in pressure observed when the CTO is 7.50 is consistent with the higher conversion in those experiments.

When *n*-hexane was used, consistent pressure profiles were also observed (refer to Figure 3). The pressure profiles for each experiment overlap each other following the same evolution, with a very sharp increase after injection, very fast evacuation steps, and clear evidence of the first sampling. Lower conversions were observed

at 550 °C compared to those obtained with *n*-hexadecane, as shown by moderate pressure increases, although a higher activity can be noticed for the pure HY sample, when compared with the E-cat at similar conditions. Reaction is negligible at 250 °C, as shown by a flat pressure profile.

A summary of the product distributions observed in the experiments with *n*-hexadecane is presented in Table 1. It can be seen that the different composition of samples M (it shows the composition of the gas phase in the reactor that is in equilibrium with the catalyst at a given reaction time) and G (it also incorporates at least part of the hydrocarbons that were adsorbed at that time) is clear. Those differences seem to be more important in the case of the higher CTO. Moreover, the conversion of *n*-hexadecane shows that the higher the CTO and the higher the reaction times, the more important the yields of the main reaction products, corresponding to LPG and gasoline lumps. Paraffins account for approximately 35 and 47% of LPG compounds at CTO of 1.15 and 7.50, respectively, with isobutane being the most important product (about 45 and 49 % of the total paraffins in LPG, respectively). The amount of coke formed is lower at the lower CTO, and as expected, it increases as a function of reaction time. The distribution of hydrocarbon types in gasoline is shown in Table 2. The selectivity does not change significantly as a function of reaction time, but the effect of CTO is quite visible. In effect, as a consequence of the higher incidence of cracking and hydrogen-transfer reactions, the importance of i-paraffins and aromatics increases when the CTO is higher, while the olefins decrease simultaneously.

A similar condition can be observed concerning the compositions of samples M and G in the conversion of *n*-hexane over the E-cat and HY zeolite, as shown in Table 3. The concentration of reactant *n*-hexane, for example, is always higher in sample M. Moreover, the yields of the main reaction products increase as a function of reaction time over E-cat, which is less active
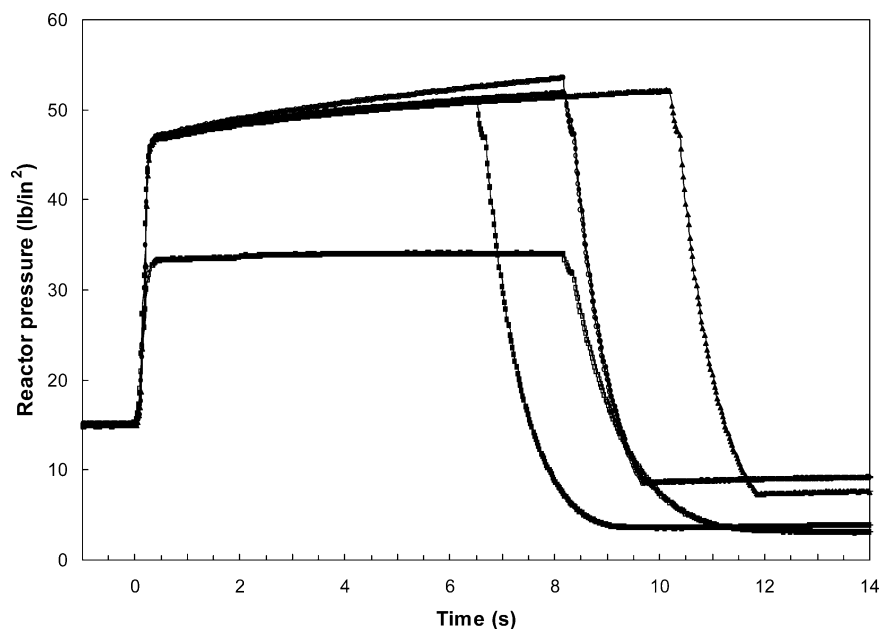
Figure 3. Pressure profiles for experiments with *n*-hexane on E-cat (temperature 550 °C, (■) 6-, (●) 8-, and (▲) 10-s reaction time; temperature 250 °C, (○) 8-s reaction time) and pure HY zeolite (temperature 550 °C, (□) 8-s reaction time).

Table 1. Composition of Samples M and G (%) and Coke Yield (%) in the Conversion of *n*-Hexadecane over E-cat (Reaction Temperature 550 °C)

	CTO 1.15			CTO 7.50		
reaction time (s)	6	8	10	6	8	10
			Sample M			
dry gases	1.6	1.9	2.2	1.4	1.9	2.2
LPG	12.0	14.9	16.8	17.4	22.0	24.9
gasoline	18.0	22.0	24.8	20.5	26.6	29.9
C13−C15	0.9	1.0	1.1	0.8	0.8	1.0
n-C16	67.5	60.2	55.1	59.9	48.7	42.0
			Sample G			
dry gases	1.7	1.9	2.3	1.6	2.0	2.3
LPG	12.3	14.4	17.1	18.9	21.7	25.5
gasoline	18.1	21.2	24.9	22.3	26.5	30.4
C13−C15	1.2	1.0	1.1	0.8	1.4	1.4
n-C16	66.7	61.5	54.7	56.4	48.4	40.4
coke yield	0.3	0.4	0.5	1.8	2.2	2.5

Table 2. Product Distribution (%) in Gasoline Products (Sample G in the Conversion of *n*-Hexadecane over E-cat. Reaction Temperature 550 °C)

	CTO 1.15			CTO 7.50		
reaction time (s)	6	8	10	6	8	10
n-paraffins	10.54	10.88	10.76	10.99	10.74	10.81
i-paraffins	29.49	30.35	31.08	36.21	36.39	38.25
olefins	46.75	45.41	44.59	38.01	37.33	35.24
naphthenics	2.86	2.88	2.85	2.45	2.49	2.42
aromatics	10.36	10.47	10.72	12.34	13.04	13.29

than the pure HY zeolite under the same conditions (see data at 8-s reaction time). Some differences between the E-cat and HY zeolite can be noticed in the product distributions presented in Table 4; for example, a higher yield of saturated products (mainly i-paraffins) was observed for the HY zeolite, which is consistent with a higher cracking and hydrogen transfer activity.

Assessment of the Adsorption Constants. For each compound in the mixture, a Henry-type equilibrium between the concentration in the gas phase and the adsorbed phase could be considered

$$q_i = K_i C_i \qquad (1)$$

Table 3. Composition of Samples M and G (%) in the Conversion of *n*-Hexane over E-cat and HY Zeolite (Reaction Temperature 550°C)

	catalyst			
	E-cat			HY zeolite
reaction time (s)	6	8	10	8
		Sample M		
dry gases	1.4	1.6	1.8	1.9
LPG	5.3	6.4	7.4	16.8
gasoline (*n*-C6 excluded)	2.8	3.3	3.8	5.0
n-C6	90.5	88.7	87.0	76.3
		Sample G		
dry gases	1.6	1.8	1.9	2.0
LPG	5.9	6.9	7.6	17.2
gasoline (*n*-C6 excluded)	3.1	3.8	3.8	5.2
n-C6	89.4	87.5	86.7	75.6

Table 4. Product Distribution (%) in Gasoline Products (Sample G in the Conversion of *n*-Hexane over E-cat and HY Zeolite. Reaction Temperature 550 °C)

catalyst	E-cat	HY zeolite
reaction time (s)	8	8
n-paraffins	7.45	9.47
i-paraffins	45.19	56.07
olefins	27.55	19.70
naphthenics	10.07	6.30
aromatics	9.52	8.43

where K_i is the apparent adsorption constant. In a simplified approach, it could be considered that all the hydrocarbons adsorbed are removed from the catalyst particles in the evacuation step, due to the strong driving force acting on the reacting mixture (pressure difference between the reactor and the much larger vacuum chamber). In that case, the difference in composition between samples M and G would allow us to know the values of q_i and C_i, thus leading to the direct calculation of K_i. However, since some hydrocarbons remain in the reactor's gas phase after evacuation (approximately 15−20% of the injected amount), it is no longer possible to accept such a statement.

For the simpler cases where no chemical reaction exists (a flat pressure profile develops), it is easy to assess the concentration of adsorbed species at any time

in the experiment as

$$q_i = \frac{(m_{i,\text{Feed}} - m_{i,R}^r)}{m_{\text{cat}}} \quad (2)$$

and then the apparent adsorption constant is

$$K_i = \frac{q_i}{C_i} = \frac{(m_{i,\text{Feed}} - m_{i,R}^r)}{m_{i,R}^r} \frac{V_R}{m_{\text{cat}}} \quad (3)$$

A similar approach for the calculations was used by Atias and de Lasa.[19] In the corresponding mass balances of other experiments performed on the same type of reactor, however, the total desorption of hydrocarbons from the catalyst was assumed in the evacuation step.[14,20]

Indeed, the assessment of K_i in this type of stirred reactor leads to apparent adsorption constants that depend not only on the temperature but also on the relationship between gas phase and solid phases and the contact time, as shown in a theoretical study by Bidabehere and Sedran.[21]

The simple procedure of eq 3 was tested with the results from experiments with n-hexane at 250 and 550 °C on the E-cat and pure HY zeolite. For the E-cat at 250 °C, the value obtained for K_{C6} was 3.9 cm³/g. It has to be considered that this value is referred to the total mass of catalyst, which indeed is composed of the zeolite, the matrix, the extra framework species from dealumination in the commercial process, and, eventually, the various catalyst additives. It is generally accepted that the adsorption in the matrix of FCC catalysts is not as strong as in the zeolite component.[10,22] Lee et al.,[10] who used a TEO microbalance, reported a value of 18 cm³/g for the case of a steamed commercial FCC catalyst. Then, if in the present case the constant is referred only to the Y zeolite component, its value is 19.9 cm³/g. Even though the dealuminated Y zeolite catalysts used in various works are not exactly the same, a comparison with reported values of Henry constants of n-hexane adsorption at the same temperature of 250 °C, assessed by means of various techniques, can be stated to show that similar magnitudes were observed. For example, from experimental data of Lee et al.[10] at 200 °C on steamed RE-Y zeolite (Si/Al n.a.), a value of 41 cm³/g can be extrapolated. From Eder and Lercher[23] a value of 21.9 cm³/g for H-FAU (Si/Al = 300) can be extrapolated from data at 50 °C. From Denayer et al.,[24] K_{C6} is 218.9 cm³/g on NaY (Si/Al = 2.7), but 50.6 cm³/g on NaUSY (Si/Al = 30), estimated from data at 300 °C. According to Bidabehere and Sedran,[4] some of these values should be considered apparent constants.

Equation 3 is no longer applicable when a chemical reaction proceeds, since the difference between the mass of reactant injected and the mass of reactant present in the gas phase at any time represents both the adsorbed and reacted masses. However, a calculation procedure can be developed based on the mass balances in two points of the evacuation step, after the desired reaction time has been reached. For the cases of time t_r (reaction time) and time t_f (when the evacuation process is stopped, refer to Figure 2), if the equilibrium is assumed between the gas and solid phases, it can be written that

$$q_i^r = K_i C_i^r \quad (4)$$

$$q_i^f = K_i C_i^f \quad (5)$$

The concentration of the species i in the reactor that is in equilibrium with the catalyst at time t_r, C_i^r, can be calculated from the chromatographic analysis of sample M, while the analogous concentration at time t_f, C_i^f, is unknown.

From the previous eqs 4 and 5, then,

$$K_i = \frac{q_i^r - q_i^f}{C_i^r - C_i^f} \quad (6)$$

Once injected, the total mass of hydrocarbons in the setup is constant and the following mass equality can be stated at times t_r and t_f, that is, at the beginning and the end of the evacuation from the reactor. Moreover, coke can be excepted, because it can be assumed that its amount does not change between times t_r and t_f:

$$m_{HC}^r = m_{HC}^f \quad (7)$$

At the end of the reaction, the hydrocarbons are distributed in the reactor between the gas phase and adsorbed on the solid catalyst; after extraction, fractions remain in the reactor (in the gas phase and adsorbed on the catalyst), and most of them are distributed between the vacuum chamber, the loop M, and the various transfer lines:

$$m_{HC,R}^r + m_{HC,\text{ads}}^r = m_{HC,R}^f + m_{HC,\text{ads}}^f + m_{HC,ML} + m_{HC,GL} \quad (8)$$

For a given species i

$$m_{i,R}^r + m_{i,\text{ads}}^r = m_{i,R}^f + m_{i,\text{ads}}^f + m_{i,ML} + m_{i,GL} \quad (9)$$

$$m_{HC,R}^r w_{i,M} + m_{\text{cat}} q_i^r MW_i = m_{HC,R}^f w_{i,R}^f + m_{\text{cat}} q_i^f MW_i + m_{HC,ML} w_{i,M} + m_{HC,GL} w_{i,G} \quad (10)$$

This expression can be reordered to know the amount of hydrocarbon i that is desorbed from the catalyst in the evacuation process:

$$m_{\text{cat}}(q_i^r - q_i^f)MW_i = m_{HC,GL} w_{i,G} + m_{HC,R}^f w_{i,R}^f - (m_{HC,R}^r - m_{HC,ML}) w_{i,M} \quad (11)$$

where the masses $m_{HC,R}^r$, $m_{HC,R}^f$, $m_{HC,GL}$, and $m_{HC,ML}$ can be calculated according to the ideal gas law, and the compositions $w_{i,M}$ and $w_{i,G}$ are known from the chromatographic analysis.

Then, after eq 11, eq 6 can be rewritten as

$$K_i = \left[\frac{m_{HC,GL} w_{i,G} + m_{HC,R}^f w_{i,R}^f - (m_{HC,R}^r - m_{HC,ML}) w_{i,M}}{(m_{HC,R}^r w_{i,M} - m_{HC,R}^f w_{i,R}^f)} \right] \times \frac{V_R}{m_{\text{cat}}} \quad (12)$$

where the only unknown variable is $w_{i,R}^f$ (that is, the composition of the gas phase that is in equilibrium with the catalyst at the final instant of the evacuation). An approximate assessment of the constants K_i could be

performed by assuming that the mass fraction $w_{i,R}^f$ (or the equilibrium concentration C_i^f) is the same as that in the vacuum chamber after evacuation, that is, $w_{i,G}$. In that case, the only unknowns are the constants K_i. This approximate assessment of the individual constants K_i with experimental data from experiments with n-hexane and n-hexadecane on the E-cat yielded some negative values, thus showing inconsistency. A sensitivity analysis was performed, changing the experimental data in the range of the experimental error ($\sim$1.5%). Although in the worst case a variation of 50% in the values of the adsorption constants was observed, negative values were still found, suggesting that the inconsistency is not due to experimental errors in the analysis of products (data set). Then, it is believed that a possible reason for this is the fact that the concentration of the more strongly adsorbed hydrocarbons in the vacuum chamber is lower than the one at equilibrium conditions in the reactor at time t_f. This phenomenon was previously observed under similar conditions for aromatic molecules with different basicity on coked USHY zeolite samples.[25]

To simplify the analysis, the different hydrocarbons can be grouped into various lumps, according to the reacting system.

Considering that the mass of hydrocarbons in the gas phase in the reactor at the final reaction time t_r ($m_{HC,R}^r$) can also be calculated from

$$m_{HC,R}^r = m_{HC,\text{Feed}} - m_{\text{Coke}} - m_{HC,\text{ads}}^r \qquad (13)$$

where $m_{HC,\text{ads}}^r$ can be known from the mass balance (eq 8), then it can be written that

$$m_{HC,\text{Feed}} - m_{\text{Coke}} - m_{HC,ML} = m_{HC,R}^f + m_{HC,\text{ads}}^f + m_{HC,GL} \qquad (14)$$

Since

$$m_{HC,\text{ads}}^f = \sum_i m_{i,\text{ads}}^f = \frac{m_{\text{cat}}}{V_R} m_{HC,R}^f \sum_i K_i w_{i,R}^f \qquad (15)$$

the adsorption parameters could be calculated by means of an optimization procedure searching for the set of values of apparent adsorption constants that minimizes the error between the right- and left-hand side of eq 14, by making use of eq 15, where K_i is calculated according to eq 12.

$$Min \left| \left(m_{HC,R}^f \left(1 + \frac{m_{\text{cat}}}{V_R} \sum_i K_i w_{i,R}^f \right) + m_{HC,GL} \right) - (m_{HC,\text{Feed}} - m_{\text{Coke}} - m_{HC,ML}) \right| \qquad (16)$$

Additionally,

$$\sum_i w_{i,R}^f = 1 \qquad (17)$$

The search for the optimum values can be restricted if some properties concerning adsorption phenomena are considered. Some examples of such restrictions are as follows: (i) the constants are positive, (ii) the adsorption of the olefins is stronger than that of the other hydro-

carbon types, and (iii) for a given hydrocarbon type, the higher the molecular weight of a compound, the more it adsorbs.

The injections of n-hexane at high temperature (550 °C) showed that conversion went up to 13.5% in the case of the E-cat (CTO 7.50, 10-s contact time) and 24.5% in the case of pure HY zeolite (CTO 1.38, 8-s contact time). These conversion values cannot be ignored to consider only a pure compound in the system. Then, according to the product distribution observed, the method proposed was applied to a system with four lumps, considering the following: paraffins other than n-hexane, olefins, aromatics, and n-hexane. The calculation was extended to all the experiments on the E-cat (three different contact times), and the results were not completely consistent because, for example, the constant for paraffins was larger than that of the olefins. This was assigned to the large differences between the relative amounts of the various groups. When only two lumps were considered, that is, paraffins (mostly n-hexane) and olefins plus aromatics (mostly olefins), the apparent adsorption constants assessed were 0.08 and 29.00 cm³/g, respectively. As expected, olefins and aromatics adsorb much more strongly than paraffins. The experiments performed on the pure HY zeolite catalyst at 550 °C yielded values of 0.01 and 71 cm³/g for the apparent adsorption constants of paraffins and olefins plus aromatics, respectively. A very large increase in the adsorption of olefins and aromatics in relation to paraffins is again observed when a chemical reaction proceeds, that is, when a mixture of hydrocarbons is in contact with the porous catalyst.

In the case of the conversion of n-hexadecane, even though a different definition of lumps could be used, four lumps were defined, according to the following chemical families, olefins, paraffins, aromatics, and n-hexadecane, that was always present in significant amounts in these experiments. The calculation was extended to all the experiments performed at a given CTO ratio, that is, three different reaction times. At both CTO ratios, the apparent adsorption constants of olefins were always much larger than those of the other lumps. In effect, K_{olef} was 22.4 and 6.2 cm³/g at CTO 1.15 and 7.50, respectively, while the constants for the other lumps tended to very small values in every case. These results confirm the observations in the experiments with n-hexane in the sense that the adsorption of hydrocarbons that adsorb more strongly when contacted pure on a catalyst surface, is selectively favored when they are taking part of a mixture with other hydrocarbons. The sensitivity analysis on the method showed that the experimental error does not induce substantial changes in the values of the constants. The differences in the values of K_{olef} with the CTO ratio could be assigned to the fact that at the lower CTO the mass transport process into the catalyst particles is facilitated by the higher hydrocarbon mass in relation to the catalyst mass in the reactor, ratifying the character of apparent of these values.[21]

To further clarify this, additional simple experiments were performed with pure toluene and n-decane and mixtures of n-hexane (60%), toluene (22%), and n-decane (18%) on the E-cat at 250 °C. These concentrations were aimed at producing similar adsorbed masses of hydrocarbons, according to the values of the individual apparent adsorption constants. Equation 3 was always used to assess the adsorption constants, since

Table 5. Apparent Adsorption Constants (cm³/g) on E-cat at 250 °C for *n*-Hexane, Toluene, and *n*-Decane Assessed from Experiments with pure Compounds and Mixture 60:22:18 (%)

	pure	mixture		
vol injected (mL)	0.1−0.3	0.10	0.15	0.20
n-hexane	3.9	0.4	1.1	3.6
toluene	9.3	8.1	10.3	11.8
n-decane	13.1	25.7	26.0	30.2

no chemical reaction proceeds, and the results are presented in Table 5. When pure, the value of the adsorption constants of decane, toluene, and *n*-hexane were essentially constant, the average values in Table 5 showing that the increasing order of adsorption is *n*-hexane < toluene < *n*-decane. However, when the constants were assessed from the experiments with the mixture, the values for *n*-decane increased by a factor of ~2, those for toluene increased moderately, and those for *n*-hexane decreased significantly. It is clear that the amount of mixture injected, or the partial pressures of the hydrocarbons in the reactor, have an impact on the assessment of the constants in the mixture.

The evidence suggests that in the competition for adsorption sites between the different components in a hydrocarbon mixture, factors other than the only adsorption process play a role; among them, the transport process inside the porous system of the catalyst is surely important.

Conclusions

The assessment of apparent adsorption constants in a catalytic system operating under conditions close to the industrial FCC practice is not trivial. *n*-Hexane and *n*-hexadecane model compounds and one equilibrium FCC catalyst were used in a modified CREC Riser Simulator allowing the analysis of a sample of the gas phase in equilibrium with the catalysts at a given reaction time, and another sample, which also includes adsorbed hydrocarbons. Mass balances and the assumption of Henry's law behavior, in combination with an optimization procedure, showed that it is possible to estimate the apparent adsorption constants of components in a complex mixture.

The values of the constants of different hydrocarbon lumps in a mixture (e.g., produced by a chemical reaction) showed that there is a clear selective enhancement in the adsorption of the hydrocarbons that adsorb more strongly (e.g., olefins) when contacted pure on a catalyst surface. The experimental evidence gathered on different catalysts and conditions suggests that the diffusive mass transport process plays an important role in the assessment of adsorption constants.

Acknowledgment

Nomenclature

m = mass (g)
MW = molecular weight
V = volume (L)
w = mass fraction
q = concentration of species adsorbed on the catalysts (mol/g)
C = concentration in the gas phase, in the reactor (mol/cm³)
K = adsorption constant (cm³/g)

Subscripts

ads = adsorbed on the catalyst
Arom = aromatics
cat = catalyst
Coke = coke on the catalyst
$C16$ = *n*-hexadecane
$C6$ = *n*-hexane
Feed = Feed tlo the reactor
G = Samplle G
GL = G sampling line, including vacuum chamber, tubing, and loop
HC = hydrocarbons
i = i component
M = sample M
ML = M sampling line, including tubing and loop
Olef = olefins
Paraff = paraffins
R = reactor

Superscripts

f = at time t_f
r = at time t_r

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