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Kinetics of the Catalytic Cracking of Paraffins at Very Short Times on Stream

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The kinetics for the cracking of *n*-heptane, *n*-decane, *n*-dodecane and *n*-tetradecane has been investigated in a reaction system in which conversion and yields can be measured at times on stream below 10 sec. Under these experimental conditions the influence of the adsorption terms in the kinetic expression is negligible. The catalyst decay is better represented by a conversion-dependent time on stream function. © 1994 Academic Press, Inc.

INTRODUCTION

It was early recognized that cracking of paraffins was catalyzed by acid sites (1, 2). In order to explain the product distribution, the carbenium ion theory (3, 4) proposed three reaction steps. *Initiation of cracking* involves the formation of an adsorbed carbenium ion from the reactant, followed by a β-scission that gives an olefin and a carbenium ion with fewer carbon atoms than the reactant. Then the second step, *chain propagation*, involves the generation of a new carbenium ion from the reactant by the transfer of a hydride ion from this to the carbenium ion remaining on the surface. Finally, *termination* of the chain occurs when the carbenium ion desorbs from the catalysts restoring the acid site. For the complex mechanism described above, it was not easy to find a detailed kinetic model. Due to this, conversion results have normally been fitted to a pseudo-first-order kinetic expression (5–8) and in this way an apparent kinetic rate constant is obtained.

Recently (9–12) the cracking of paraffins has been explained assuming two different cracking mechanisms. One of them involves the mechanism described above and corresponds to bimolecular hydride transfer followed by β-scission. The other, which is monomolecular, involves attack on a C–C bond by a H^+ from the catalyst to form a carbonium ion, which then cracks, giving a paraffin in the gas phase and the remaining fragment staying on the catalyst as a carbenium ion. In this monomolecular mechanism, when cracking has occurred and the smaller carbenium ion is formed, it can desorb as an olefin, while restoring the H^+ of the catalyst, and then the acid site is ready to start a new monomolecular cracking event. However, it may also occur that before desorbing, the carbenium ion can abstract a hydride ion from a reactant molecule and then the β-scission mechanism follows. If one accepts the dual mechanisms, it appears that the relative contribution of each depends on the relative rates of carbenium ion desorption and hydride transfer. These, in turn, depend on reaction conditions and the nature of the catalyst. High temperatures and zeolites with high framework Si/Al ratios and/or small pores favor monomolecular cracking mechanism, even though both mechanisms still work. In the case of the large pore Y zeolite, despite the coexistence of mono- and bimolecular cracking, a first-order kinetic model has been applied (13).

Riekert and Zhou (14) have established the contributions of the mono- and bimolecular cracking mechanisms by considering the equilibrium adsorption for all the species. They conclude that at reaction temperatures higher than 400°C and reactant partial pressures above 10 mbar, the reaction can be described by a first-order kinetic expression. Others (15–18) have fitted their kinetic results to a Langmuir–Hinshelwood expression, considering only the monomolecular mechanism. They justified the use of this kinetic expression by the good fitting of the experimental results, and also because they did not observe an induction period during the cracking of paraffins. Groten *et al.* (19) take the two cracking mechanisms into account in the kinetic expression, considering protolytic cracking, and the β-scission as the controlling steps. They conclude that the kinetic term corresponding to monomolecular cracking is able to simulate the contribution of the two mechanisms within the limits of experimental error.

It is evident to us that the efforts made by different authors to improve the fundamental knowledge of catalytic cracking can become fruitless if kinetic data are ob-

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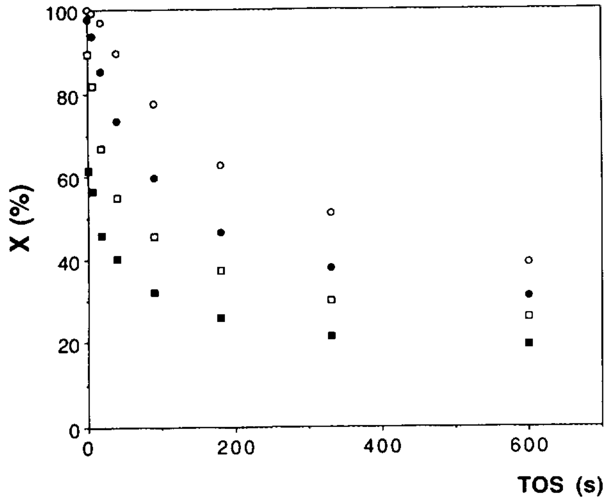

FIG. 1. Influence of time on stream over instantaneous conversion in *n*-Decane cracking. Values of W/F_{A_0} (kg s mol^{-1}) (○) 13.008, (●) 6.524, (□) 3.262, (■) 1.624.

tained when the catalyst has lost most of its activity by deactivation. Indeed, if one considers that large pore zeolites deactivate within a few seconds, and also that in FCC units the time on stream (TOS) is below 5 s, it is possible to deduce that the most convenient way to operate is not by taking samples at TOS of 60 s, and even higher, as is done in most works. Even in those cases in which cumulative conversions are considered, problems can arise when kinetic models are applied if the decay is very fast.

In this work we have studied the cracking of *n*-heptane, *n*-decane, *n*-dodecane, and *n*-tetradecane on a USY zeolite while measuring instantaneous conversion at very short times on stream by means of a multisampling computer-controlled valve located at the end of the reactor. With these data a kinetic and decay expression has been developed and compared with previously reported kinetic equations for paraffin cracking.

THEORY

In this section the models used to fit the experimental results are described.

(*A*) *First Order Model*

For a simple first-order kinetic model the expression can be written

$$\frac{\partial X}{\partial (W/F_{A_0})} = k_t \frac{(1 - X)}{(1 + \varepsilon X)} C_{A_0} \phi, \qquad [1]$$

in which X is the degree of conversion for the paraffin feed, W is the weight of catalyst, F_{A_0} is the molar flow rate of the paraffin, k_t is the global apparent kinetic rate constant, ε is the volume expansion coefficient, C_{A_0} is the concentration of the reactant in the inlet of the reactor, and ϕ is the catalyst activity at each time on stream.

A model like this does not take into account the adsorption of reactants and products; or even better, it considers that the population of surface adsorbed molecules is very low ($1 \gg K_a(1 - X)$). Even though some authors (13, 14) do consider that this assumption can be applied to the catalytic cracking of paraffins, especially at higher reaction temperatures, others (15–19) believe that the adsorption terms have to be included in the kinetic rate expression.

(*B*) *Langmuir–Hinshelwood Model*

For a cracking mechanism that is exclusively monomolecular, Abbot and Wojciechowski (15) have shown that if a competitive adsorption between the reactant molecule and the cracking products, especially olefins, exists and the controlling step is the protolytic cracking step, then the kinetic expression becomes

$$\frac{\partial X}{\partial (W/F_{A_0})} = \frac{A(1 - X)/(1 + \varepsilon X)}{1 + B(1 - X)/(1 + \varepsilon X)} C_{A_0} \phi, \qquad [2]$$

TABLE 1

Parameters of First-Order and Langmuir–Hinshelwood Kinetic Models with Independent Decay Equation for *n*-Decane Cracking

	Model: Eqs. [1], [3]				Model: Eqs. [2], [3]		
	TOS ≥ 0 s	TOS ≥ 39 s	TOS ≥ 90 s		TOS ≥ 0 s	TOS ≥ 39 s	TOS ≥ 90 s
k_t (m^{3}s^{-1}kg^{-1})	0.395	0.540	0.563	A (m^{3}s^{-1}kg^{-1})	0.207	0.137	0.142
				B	−0.945	−0.999	−1.000
G (s^{-1})	0.097	0.193	0.199	G (s^{-1})	0.085	0.040	0.042
N	0.641	0.611	0.617	N	0.832	0.966	0.964
Σ (residuals)^2	0.123	0.118	0.107	Σ (residuals)^2	0.030	0.008	0.005

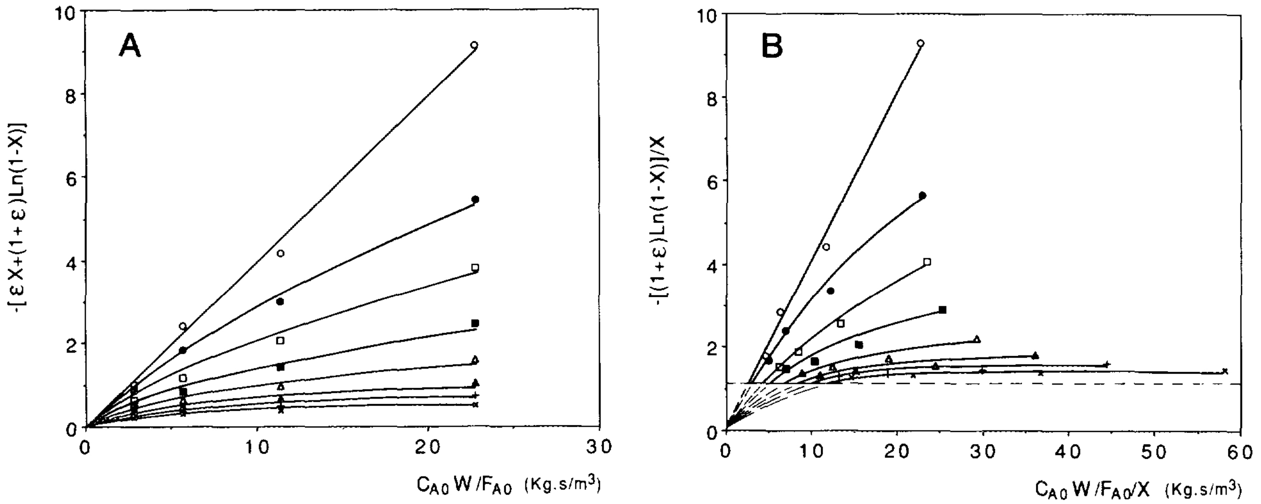

FIG. 2. Plots of Eq. [7] (A) and Eq. [8] (B) for *n*-decane cracking. Times on stream (s): (○) 0, (●) 6, (□) 18, (■) 39, (△) 90, (▲) 180, (+) 330, (×) 600.

in which *A* and *B* are kinetic parameters which include kinetic rate and adsorption constants.

(*C*) *Catalyst Decay Models*

In the case of Y zeolites which are of commercial interest in catalytic cracking, their activity strongly decays with TOS, and therefore, a decay function which relates activity with time on stream has to be introduced.

Abbot and Wojciechowski (15–18) recommend to use an independent decay equation, in the terminology of Khang and Levenspiel's (20), derived from the time on stream theory (21),

$$\phi = (1 + Gt)^{-N} \qquad [3]$$

in which *G* and *N* are decay parameters and *t* is the time on stream.

However, the use of an independent decay model is not consistent with a kinetic model in which the product olefins are considered to be strongly adsorbed, especially if one considers that olefins do play an active and important role for catalyst decay. Due to this, we believe that a more realistic decay model should be used for dependent decay,

$$\frac{\partial \phi}{\partial t} = -K_{\mathrm{md}}\phi^{m}X, \qquad [4]$$

where K_{md} and m are the decay parameters.

A model like this is consistent with the observed fact that a direct relationship exists between the amount of coke, which is a secondary product in paraffin cracking (1, 22), and catalyst decay. Equation [4] can also be explained

TABLE 2

Parameters of Eqs. [7] and [8] for All Reactants Used in This Study

Reactant	k_t (m³s⁻¹kg⁻¹)	A (m³s⁻¹kg⁻¹)	B	ε^a
n-Heptane	0.122	0.138	0.253	0.097
n-Decane	0.396	0.404	0.138	0.141
n-Dodecane	0.556	0.547	−0.171	0.183
n-Tetradecane	0.734	0.724	−0.152	0.222

[a] Calculated from experimental product distribution.

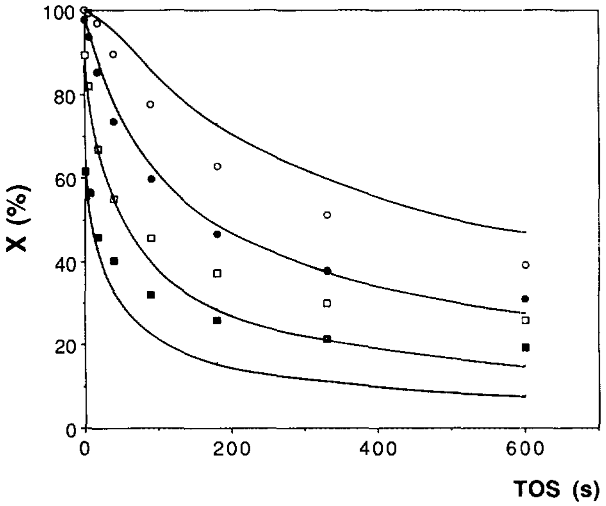

FIG. 3. Experimental and theoretical instantaneous conversion in decane cracking. Symbols as in Fig. 1. (—) Model Eqs. [1], [3].

TABLE 3

Parameters of Pseudo-First-Order Kinetic Equation and Independent or Dependent Decay Model

	Reactant							
	C_7		C_{10}		C_{12}		C_{14}	
	Ind.	Dep.	Ind.	Dep.	Ind.	Dep.	Ind.	Dep.
k_t ($m^3s^{-1}kg^{-1}$)	0.115	0.108	0.395	0.375	0.640	0.570	0.830	0.775
G or K_{md} (s^{-1})	0.079	0.062	0.097	0.110	0.127	0.102	0.044	0.078
N or m	0.421	2.38	0.641	2.14	0.659	1.94	1.010	1.72
Σ (residuals)^2	0.037	0.017	0.123	0.007	0.168	0.015	0.298	0.050

from the model proposed by Froment and co-workers (23, 24). These authors have related decay with coke through the expressions

$$\frac{\partial C_C}{\partial t} = r_C^0 \phi, \qquad [5]$$

$$\phi = \exp(-\alpha C_C), \qquad [6]$$

where C_C is the amount of coke formed at each time on stream (t), r_C^0 is the rate of coke formation in absence of decay and α is an adjustable parameter.

From Eqs. [5] and [6] and if a first order rate for coke formation is assumed, the equation [4] for the particular case in which $m = 2$ is obtained. Then, our decay function implies that the relationship between catalyst activity and the secondary products responsible for catalyst decay is exponential.

In Eqs. [1], [2], and [4], X represents the instantaneous conversion degree, and the integration of Eqs. [1] and [2] done in a coupled way with the decay model makes it possible to calculate the instantaneous conversion at the outlet of the reactor. Then, if one determines experimentally the instantaneous conversion at different TOS and different contact times, the model can be directly tested.

EXPERIMENTAL

Materials

The USY zeolite catalyst was prepared by exchanging an SK-40 NaY zeolite with NH_4^+ at 80°C. Then the zeolite was steam-calcined at 550°C for 3 h followed by NH_4^+ exchange-calcination (500°C) twice. The final unit cell size of the catalyst was 24.46 Å, the Na_2O content being 0.106 wt%. The zeolite was pelletized, crushed, and sieved, and particles of size 0.30–0.50 mm were used.

n-Heptane, *n*-decane, *n*-dodecane, and *n*-tetradecane (99%+) were obtained from Aldrich and were used without further purification. N_2 (99.999% purity) was used as a carrier gas.

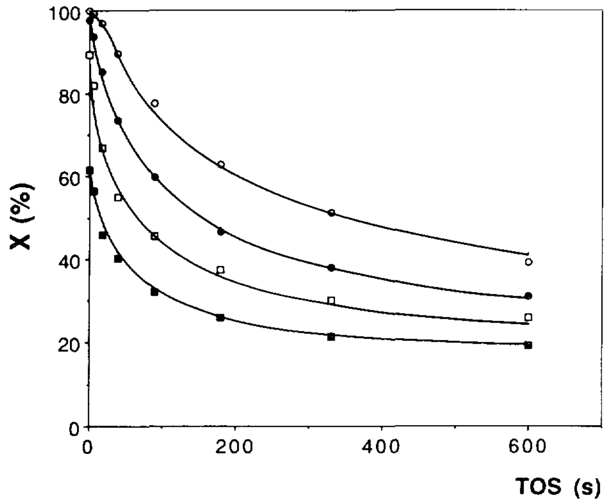

FIG. 4. Experimental and theoretical instantaneous conversion in decane cracking. Symbols as in Fig. 1. (—) Model Eqs. [1], [4].

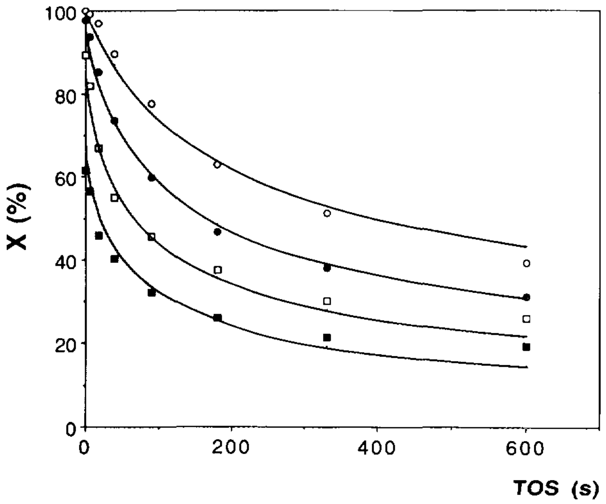

FIG. 5. Experimental and theoretical instantaneous conversion in Decane cracking. Symbols as in Fig. 1. (—) Model Eqs. [2], [3].

TABLE 4

Parameters of Langmuir–Hinshelwood Kinetic Equation Coupled with Independent Decay Model

	Reactant			
	C_7	C_{10}	C_{12}	C_{14}
A ($m^3s^{-1}kg^{-1}$)	0.090	0.207	0.348	0.428
B	−0.340	−0.945	−1.000	−1.000
G (s^{-1})	0.073	0.085	0.085	0.046
N	0.445	0.832	0.955	1.209
Σ (residuals)^2	0.032	0.030	0.028	0.070

Reaction Procedure

The experiments were performed in a fixed bed continuous glass reactor of 11 mm internal diameter and 300 mm length equipped with a coaxial thermocouple for measuring the temperature of the catalytic bed. The reactor was heated in an electric furnace. The zeolite was diluted with SiO_2 (Basf), the length of the catalyst bed being kept constant. The N_2/HC molar ratio was always 9, the HC flow being 7.7×10^{-6} mol · s^{-1}. The reactor exit is connected to a multisampling computer controlled heated valve (0.25 cm^3/loop). A hydrocarbon detector is located at the outlet of the valve in order to detect in a very precise way the moment when hydrocarbon fills the first loop. This moment is considered the zero reaction time, and the sample is automatically kept in the first loop. The rest of the loops were automatically filled, as programmed, at 6, 18, 39, 90, 180, 330, and 600 s TOS. After the experiment was finished the samples were separated in a 100-m capillary column (Supelco-Petrocol) and analyzed using two detectors (TCD and FID). The contact time was varied between 0.84 and 13.01 kg mol^{-1} s by changing the weight of the catalyst. Several experiments were duplicated and the reproducibility was excellent.

The fitting of the experimental instantaneous conversion was carried out by minimizing the sum of the squares of the errors or residuals (least-square technique) by means of Marquardt's algorithm.

RESULTS AND DISCUSSION

With the experimental setup described above it is possible to determine the instantaneous conversion at the exit of the reactor, and by taking samples at different times the evolution of instantaneous conversion with time on stream can be followed. As an example, the results obtained for *n*-decane are given in Fig. 1. From the curve it is possible to see that in a very few seconds the catalyst has lost most of its activity. Therefore it becomes clear that the results obtained at times on stream lower than 20 s are crucial if reliable kinetic rate constants in the absence of decay are to be obtained. This can be visualized from the results presented in Table 1, in which the kinetic parameters have been calculated from Eqs. [1] and [3], and [2] and [3] using shorter and shorter times on stream.

From the above results, and regardless of the kinetic model used, it becomes evident that different kinetic parameters are obtained when conversions at shorter TOS are used for the fitting.

Since in our case we dispose of conversions at zero time on stream and at different contact times, it should be possible to fit the different cracking kinetics models

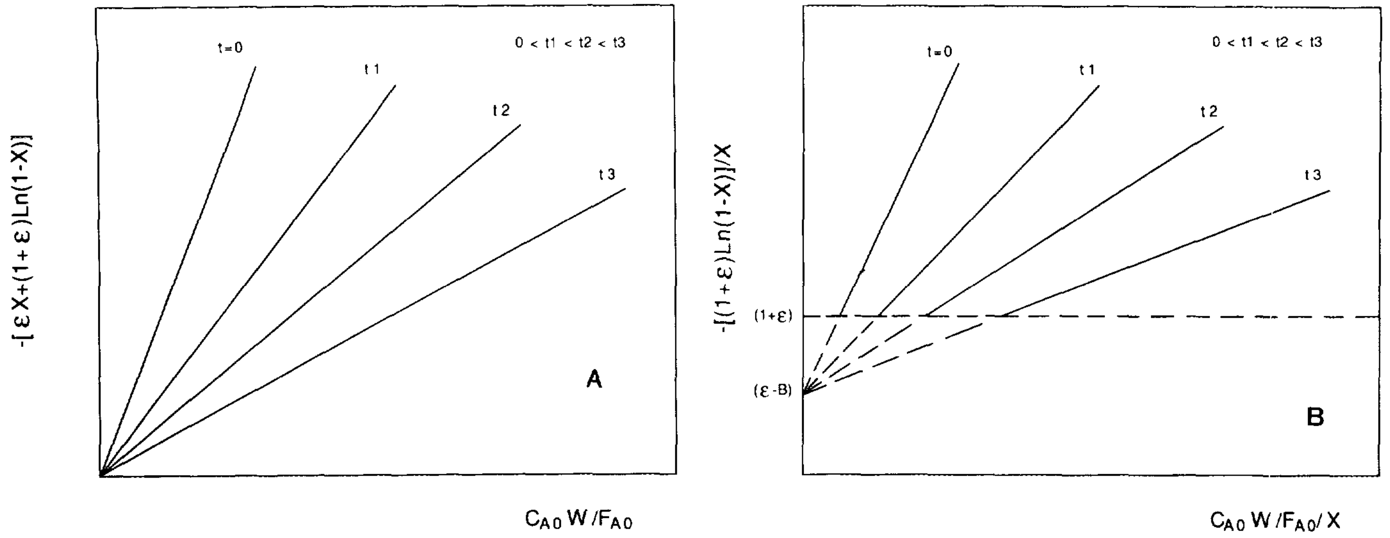

FIG. 6. Theoretical behavior for paraffin cracking in independent decay model: (A) first-order kinetics, (B) Langmuir–Hinshelwood kinetics.

with these data without the need for introducing decay expressions. In other words, when using conversion at zero TOS we can consider in Eqs. [1] and [2] that $\phi = 1$. Then by integration of these equations the following expressions were obtained,

$$-\varepsilon X|_{\mathrm{TOS}=0} - (1+\varepsilon)\ln(1 - X|_{\mathrm{TOS}=0}) = k_t C_{A_0}\frac{W}{F_{A_0}} \qquad [7]$$

$$\frac{-(1+\varepsilon)\ln(1 - X|_{\mathrm{TOS}=0})}{X|_{\mathrm{TOS}=0}} = A\, C_{A_0}\frac{W}{F_{A_0} X|_{\mathrm{TOS}=0}} + (\varepsilon - B), \qquad [8]$$

for pseudo-first-order kinetics [7] and Langmuir–Hinshelwood kinetics [8] with reactant and products competing for adsorption sites.

Plots from Fig. 2 show that when X at TOS = 0 are considered very good straight lines are obtained if our experimental results are fitted to both models. However, this was not the case when x at TOS = 0 were considered. Thus we have to conclude that, from a kinetic point of view, both a pseudo-first-order model and a Langmuir–Hinshelwood model fit the results and therefore the contribution of the adsorption term may have a marginal influence under the experimental conditions used here.

From the slope of the straight lines obtained when fitting the experimental results to Eqs. [7] and [8] it is possible to calculate k_t, A, and B. The values obtained for the different hydrocarbons are given in Table 2. Following the theoretical discussion in Ref. (15), parameter B must be negative in reactions in which the reaction products (olefins) are more strongly adsorbed than the reactant. This is not seen in our case for all reactants, and furthermore while k_t and A give very close values, the value of B is small. These results suggest again that the adsorption term in Eq. [2] has little significance, under our experimental conditions.

Fitting Results Affected by Catalyst Decay

After showing that the kinetic model from Eq. [1] can be applied to the cracking of paraffins, we discuss here what decay model, dependent or independent, should be considered, as were developed by Viner and Wojciechowski for cumene and gasoil cracking (26, 27).

In our first publications on *n*-heptane cracking (25) we used the kinetic equation [1] and the independent decay model proposed in the literature (21), and the fittings obtained were not good enough. Similarly when the experimental instantaneous conversions obtained here at different TOS are fitted to a pseudo-first-order kinetics (Eq. [1]) coupled with the independent decay model (Eq. [3]), Fig. 3 shows that the fit is not adequate for *n*-decane, and the same is true for the other reactants. However, as soon as a catalyst decay dependent function is added (Eq. [4]), the fit strongly improves and a very good fit of the experimental results is obtained (Table 3 and Fig. 4).

When a Langmuir–Hinshelwood kinetic model coupled with an independent catalyst decay (Eq. [3]) function is used, a good fit is also observed (Fig. 5 and Table 4). However, one has to consider that one additional fitting parameter is used in this case, and it is not surprising to produce a good fit with a model containing four parameters. Moreover, the A and B parameters presented in Table 4 and calculated considering conversion data at different TOS are different from those presented in Table 2, which were calculated from conversions at zero TOS and different contact times. On the other hand, the k_t parameters calculated using the dependent decay model or conversion data at zero TOS are very similar (Tables 2 and 3). From all this, and also from a conceptual point of view, it looks more logical to use a conversion-dependent decay function since, as is generally accepted, secondary reactions of olefins are responsible for coke formation and consequently for catalyst decay.

In order to further discuss this, the theoretical behavior of the catalyst expected with independent deactivation is given in Fig. 6 for the two kinetic rate expressions. In both cases straight lines with positive slopes are generated at different TOS, and from the values of the slopes one may calculate the values of k_t or A at different TOS. Moreover, when a pseudo-first-order kinetic equation is used, all straight lines go to the zero origin, while for the Langmuir–Hinshelwood model all straight lines tend to the value $(\varepsilon - B)$. It is possible to deduce that in this second case the minimum value for the Y axis $(1 + \varepsilon)$ is obtained at zero conversion.

Then, if straight lines are predicted in Fig. 6 when an independent decay model is assumed regardless of the kinetic model, this does not correspond to the observed reality. Indeed, results from Fig. 2 for *n*-decane cracking clearly show that the behavior is not linear for TOS > 0 regardless of the kinetic model used. The same is observed for the other hydrocarbons used in this work. This is a confirmation that the independent decay model is not the most adequate to describe catalyst deactivation during cracking of paraffins on the USY zeolite under our reaction conditions.

CONCLUSIONS

It can be concluded that cracking of paraffins on a USY zeolite at high reaction temperature, 500°C, and low hydrocarbon partial pressure can be represented by a pseudo-first-order kinetic rate expression. The influence of the adsorption terms under these experimental conditions is negligible. The catalyst decay is better represented by a conversion-dependent time on stream function, and an independent decay function does not correspond well with observed reality. Finally, it has been shown that cracking behavior on fast deactivating catalysts should be discussed on the basis of conversions obtained at very short times on stream. Then, expending time and effort in designing more suitable reaction systems is strongly recommended if cracking results are to be used to discuss fundamentals and to predict hydrocarbon cracking behavior in FCC units.

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