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# Catalytic Cracking of Cumene in a Riser Simulator: A Catalyst Activity Decay Model

S. Al-Khattaf<sup>†</sup> and H. de Lasa<sup>\*‡</sup>

Chemical Reactor Engineering Centre, Faculty of Engineering Science, University of Western Ontario, London, Ontario, Canada N6A 5B9, and Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

The present study reports the catalytic cracking of cumene using a novel CREC riser simulator. Two sizes of zeolite crystals (0.4 and 0.9  $\mu\text{m}$ ) are employed in the experiments. The goal is to develop and test, under relevant reaction conditions for FCC (temperature, contact time, reactant partial pressure, catalyst/oil ratio), a new catalytic activity decay model based on "reactant conversion". Kinetic and decay model parameters are estimated using regression analysis. Activation energies, deactivation constants, and Arrhenius preexponential constants are calculated with their respective confidence intervals. The lack of transport constraints on the cumene molecules inside the zeolites is confirmed by evaluating a modified Thiele modulus and effectiveness factors.

## Introduction

Catalyst deactivation in fluid catalytic cracking (FCC) can take place as a result of several factors. Catalyst pellets can lose its shape or mass as a result of attrition and high temperatures (sintering). Catalyst poisoning can also take place given the effect of impurities contained in the feedstock. Typical contaminants are hydrocarbons containing S, N, O, Ni, and V.<sup>1–3</sup> However, under normal FCC conditions, coke is the most important factor affecting catalyst activity. As catalytic reactions progress, coke deposits on the catalyst surface, covering active sites and leading to catalyst decay. In this respect, important modeling efforts have been addressed to the modeling of catalyst decay due to coke.

A first approach to modeling catalyst deactivation is based on a time-on-stream (TOS) decay model. This empirical model assumes that the coking rate is independent of reactant composition, extent of conversion, and hydrocarbon space velocity.<sup>4</sup> In this respect, classical decay models include an exponential decay law,  $\varphi = \exp(-\alpha t)$ ,<sup>5</sup> and a power decay law,  $\varphi = t^{-n}$ . More recent contributions consider modified exponential functions,  $\varphi = \exp(-\alpha t^n)$  with  $n = 0.4$  and  $n = 0.5$ .<sup>6</sup> Regarding TOS models, Szepe and Levenspiel<sup>8</sup> showed that decay functions can be derived by assuming that the rate of activity decay is a function of the number of active sites involved in the deactivation event. In this respect,  $d\varphi/dt = -k_d\varphi^n$  and  $d\varphi/dt = -k_{d1}C_{go}^2\varphi$  were suggested.<sup>8</sup> Wojciechowski<sup>9</sup> considered the integration of  $d\varphi/dt = -k_d\varphi^n$ , which yielded  $\varphi = [1 + k_{d1}t(n-1)]^{-N}$ .

A second approach to catalyst decay involves a catalyst activity decay function related to the coke content. Several relations of this type have been reported, such as  $\varphi = \exp(-\delta C_c)$ ,  $\varphi = 1/(1 + \delta C_c)$ ,  $\varphi = 1/(1 + \delta C_c)^2$ ,  $\varphi = 1 - \delta C_c$ , and  $\varphi = (1 - \delta C_c)^2$ .<sup>10,11</sup> With the same objective, a number of two parameter models based on the coke concentration have been proposed as follows: (a)  $\varphi = 1/(1 + \delta C_c^n)$ ,<sup>12</sup> (b)  $\varphi = \varphi_R + (1 - \varphi_R)$

$\exp(-\delta C_c)$ ,<sup>13</sup> (c)  $\varphi = (B + 1)/[B + \exp(\delta C_c)]$ ,<sup>14</sup> and (d)  $d\varphi/dC_c = F\varphi + G\varphi(1 - \varphi)$ .<sup>15</sup> Corma et al.,<sup>16</sup> studying catalytic cracking of paraffins, argued about interrelating activity decay, coke on catalyst, and reactant conversion using (a)  $d\varphi/dt = -k_{md}\varphi^m C_c$  and (b)  $dC_c/dt = r_c^0\varphi$ , which is equivalent to  $\varphi = \exp(-\delta C_c)$  for  $m = 2$  and a first-order rate of coke formation.

Thus, although the mechanism of coke formation is not yet well understood and there is still debate about suitable decay models, the present study proposes a sound approach for catalyst deactivation with a decay function based on "reactant conversion". This decay model is tested in the present study in the context of the catalytic cracking of cumene in a novel CREC riser simulator.

## Modeling Cumene Cracking in the CREC Riser Simulator

Cumene cracking is a first-order reaction.<sup>17</sup> Its disappearance in the riser simulator can be represented by the following species balance equation

$$-\frac{V}{W_c} \frac{dC_A}{dt} = \eta k_{in} \varphi_{in} C_A \quad (1)$$

where  $C_A$  represents the cumene concentration in the riser simulator ( $\text{kmol}/\text{m}^3$ ),  $V$  is the volume of the riser ( $45 \times 10^{-6} \text{ m}^3$ ),  $W_c$  is the mass of catalyst ( $0.81 \times 10^{-3} \text{ g}$ ),  $t$  is the reaction time in seconds,  $\eta$  is the effectiveness factor,  $\varphi_{in}$  is the intrinsic deactivation function, and  $k_{in}$  is the intrinsic rate constant in  $\text{m}^3/(\text{kg}_{\text{cat}} \text{ s})$ .

Moreover, the concentration of cumene,  $C_A$ , can be expressed by the relationship

$$C_A = \frac{y_A W_{hc}}{MW_A V} \quad (2)$$

where  $y_A$  represents the cumene mass fraction,  $W_{hc}$  is the total mass of hydrocarbons inside the riser ( $0.16 \times 10^{-3} \text{ kg}$ ), and  $MW_A$  is the cumene molecular weight ( $120 \text{ kg}/\text{kmol}$ ).

\* Corresponding author.

<sup>†</sup> King Fahd University of Petroleum & Minerals.

<sup>‡</sup> University of Western Ontario.

Furthermore,  $k_{\text{in}}$  can be expressed using an Arrhenius relation as  $k_{\text{in}} = k_0 \exp(-E_{\text{R}}/RT)$ . Then, eq 1 can be written as

$$-\frac{V}{W_{\text{c}}} \frac{dy_{\text{A}}}{dt} = \eta k_0 \exp\left(-\frac{E_{\text{R}}}{RT}\right) \varphi_{\text{in}} y_{\text{A}} \quad (3)$$

In addition, to reduce parameter cross-correlation, it is common to adopt the following form of eq 3

$$-\frac{V}{W_{\text{c}}} \frac{dy_{\text{A}}}{dt} = \eta k_0 \exp\left[-\frac{E_{\text{R}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \varphi_{\text{in}} y_{\text{A}} \quad (4)$$

where  $T_0$  represents the average temperature used in the reaction experiments.

It can be observed that eqs 1 and 4 account for the possible diffusion transport limitations on the cracking reaction. In this respect, an effectiveness factor ( $\eta$ ) has to be used to describe the effect of diffusion on the cracking reaction.<sup>17</sup> Moreover, to rigorously model this problem, an effectiveness factor for a FCC catalyst can be evaluated as follows<sup>18</sup>

$$\eta = \frac{\tanh(H)}{H} \quad (5)$$

where  $H$  is the modified Thiele modulus, which is defined as

$$H = \frac{1}{a_{\text{ext}}} \sqrt{\frac{(n+1)k_{\text{in}}\rho_{\text{c}}\varphi_{\text{in}}C_{\text{A}}^{n-1}}{2D_{\text{eff}}}} \quad (6)$$

where  $\rho_{\text{c}}$  represents the catalyst density in  $\text{kg}/\text{m}^3$ ,  $n$  is the reaction order (set to 1 for cumene cracking),  $k_{\text{in}}$  is the intrinsic kinetic rate constant in  $\text{m}^3/(\text{kg}_{\text{cat}} \text{ s})$ ,  $\varphi_{\text{in}}$  is the intrinsic deactivation function, and  $a_{\text{ext}}$  is the catalyst external surface area in  $1/\text{m}$ .

However, for the case of the catalytic cracking of cumene, some important clarifications have to be introduced in eq 6.<sup>19</sup> One important consideration is that, for a first-order reaction, the Thiele modulus becomes independent of the reactant concentration. Another important consideration concerns the characteristic parameter used to calculate  $a_{\text{ext}}$ . Given that essentially all of the cracking reactions take place in the zeolite crystal with little influence of the matrix,  $a_{\text{ext}}$  should be defined using the characteristic dimension of the crystal,  $L$ . Thus, approximating the crystal geometry with an equivalent sphere,  $a_{\text{ext}} = L/6$ , and eq 6 becomes

$$H = \frac{L}{6} \sqrt{\frac{k_{\text{in}}\varphi_{\text{in}}\rho_{\text{c}}}{D_{\text{eff}}}} \quad (7)$$

where  $\rho_{\text{c}}$  is the zeolite density ( $825 \text{ kg}/\text{m}^3$ ).

Regarding the various kinetic parameters in eq 7, one very relevant parameter is  $k_{\text{in}}$ . This so-called intrinsic kinetic constant could be hypothesized to change with temperature following an Arrhenius expression,  $k_{\text{in}} = k_0 \exp(-E_{\text{R}}/RT)$ , where  $k_0$  and  $E_{\text{R}}$  represent the frequency factor and the energy of activation of the intrinsic cumene cracking, respectively.

Diffusivity in zeolites can be represented by the Eyring equation as follows

$$D_{\text{eff}} = D_0 \exp\left(\frac{-E_{\text{D}}}{RT}\right) \quad (8)$$

where  $E_{\text{D}}$  is the diffusion activation energy.  $E_{\text{D}}$  is estimated to be around  $26 \text{ kJ}/\text{mol}$ , and  $D_0$  is approximately  $3.2 \times 10^{-10} \text{ m}^2/\text{s}$ .<sup>20</sup> It has to be stressed that this estimation is based on diffusivity measurements in faujasites performed with aromatic species with molecular sizes in the cumene range. For example, the value assigned to cumene falls in an intermediate range with respect to the values measured for xylene and 1,3,5-triisomethylbenzene.<sup>21</sup>

One important matter in accounting for catalyst deactivation is to consider in eq 7 a deactivation function,  $\varphi_{\text{in}}$ . One classical approach to describing catalyst decay is to consider catalyst decay as a function of time on stream

$$\varphi_{\text{in}} = \exp(-\alpha t) \quad (9)$$

where  $\alpha$  is a constant and  $t$  is the time the catalyst is exposed to a reactant atmosphere (time on stream).

By substituting eq 9 into eq 4, setting  $\eta = 1$ , and integrating the resulting equation, one obtains

$$y_{\text{A}} = \exp\left[-\frac{W_{\text{c}}k_0 \exp\left[-\frac{E_{\text{R}}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{V\alpha}(1 - \exp(-\alpha t))\right] \quad (10)$$

In addition, it is demonstrated in the present study that a catalyst activity decay function can be conveniently expressed as a function of converted reactant. First, coke formation can be postulated to take place as a proportion of hydrocarbon conversion. This approach is sound if one considers that coke is mainly the result of the primary cracking reaction steps. This means that eq 3 can be modified to express the rate of coke formation using a stoichiometric number,  $\nu_{\text{c}}$ , and the corresponding molecular weight ratio as follows

$$\frac{dC_{\text{c}}}{dt} = \left(\nu_{\text{c}}k\varphi y_{\text{A}}\frac{W_{\text{c}}}{V}\frac{\text{MW}_{\text{c}}}{\text{MW}_{\text{A}}}\right) \quad (11)$$

where  $k$  is the reaction rate constant of cumene cracking and  $C_{\text{c}}$  is the coke mass fraction based on the catalyst weight.

Equation 11 can be divided by eq 3 to give

$$\frac{dC_{\text{c}}}{dy_{\text{A}}} = -\nu_{\text{c}}\frac{W_{\text{hc}}}{W_{\text{c}}}\frac{\text{MW}_{\text{c}}}{\text{MW}_{\text{A}}} \quad (12)$$

Because the right side of eq 12 is assumed to be constant, eq 12 can be written as

$$\frac{dC_{\text{c}}}{dy_{\text{A}}} = A \quad (13)$$

where  $A$  lumps a group of constant parameters.

By integrating eq 13 between 0 and  $C_{\text{c}}$  and between 1 and  $y_{\text{A}}$ , the following equation is obtained

$$C_{\text{c}} = A(1 - y_{\text{A}}) \quad (14)$$

with

$$A = -\frac{\nu_{\text{c}}W_{\text{hc}}\text{MW}_{\text{c}}}{W_{\text{c}}\text{MW}_{\text{A}}} \quad (15)$$

**Table 1. Properties of the Small and Large Zeolites of This Study**

	small zeolite	large zeolite
Na <sub>2</sub> O (wt %)	4.1	0.25
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (mol/mol)	5.6	5.7
unit cell size (Å)	24.49	24.51
crystal size (μm)	0.4	0.9

**Table 2. Properties of CAT-SC and CAT-LC Catalysts Used in This Study**

	CAT-SC <sup>a</sup>	CAT-LC <sup>b</sup>
unit cell size (Å)	24.28	24.28
BET surface area (m <sup>2</sup> /g)	148	155
Na <sub>2</sub> O (wt %)	negligible	negligible
crystal size (μm)	0.4	0.9

<sup>a</sup> Catalyst with small crystals. <sup>b</sup> Catalyst with large crystals.

Once this first step of relating the conversion of reactant to the coke fraction is established, the next step in the analysis is to consider a catalyst activity decay function based on the coke concentration

$$\varphi = \exp(-\delta C_c) \quad (16)$$

However, given the relationship between the coke concentration on the catalyst,  $C_c$ , and the weight fraction of cumene,  $y_A$ , as given by eq 14, one obtains

$$\varphi = \exp[-\lambda(1 - y_A)] \quad (17)$$

where  $\lambda = A\delta$ .

This result can be substituted into eq 4. Then, setting  $\eta = 1$ , the following equation describing the rate of reactant consumption is obtained

$$-\frac{V}{W_c} \frac{dy_A}{dt} = K_0 \exp\left[\frac{-E_R}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \exp[-\lambda(1 - y_A)] y_A \quad (18)$$

Thus, the catalyst activity decay model based on reactant conversion given by eq 18 involves three parameters  $K_0$ ,  $E_R$ , and  $\lambda$ . These three parameters can be defined using a number of experiments in the riser simulator, as discussed in the upcoming section Experimental Procedures.

## Experimental Procedures

Cumene was employed in the present study as a model reactant compound. Regarding the FCC catalysts, commercially available Y zeolites, with small and large crystals, manufactured by the Tosoh company, were used. The properties of these zeolites are reported in Table 1.

These Na zeolites were ion-exchanged with NH<sub>4</sub>NO<sub>3</sub> to replace the sodium cation with NH<sub>4</sub><sup>+</sup>. Following this, NH<sub>3</sub> was removed, and the H form of the zeolites was spray-dried using kaolin as the filler and silica sol as the binder. The resulting 60-μm catalyst particles had the following composition: 30 wt % zeolite, 50 wt % kaoline, and 20 wt % silica sol. The process of sodium removal was repeated for the pelletized catalyst. Following this step, the catalyst was calcined for 2 h at 600 °C. Finally, the fluidizable catalyst particles (60-μm average size) were treated with 100% steam at 760 °C for 5 h. Table 2 reports the main properties of the catalysts following pretreatment. The unit cell size was determined by X-ray diffraction following ASTM stand-

ard D-3942-80. Surface area was measured using the BET method. It can be observed that the initial zeolite unit cell size of 24.5 Å was reduced following steam treatment for both zeolites to around 24.28 Å.

The catalytic activity of the Y zeolite catalyst prepared using the various techniques described above was measured in a riser simulator using cumene as the hydrocarbon feedstock. The riser simulator is a novel bench-scale apparatus with internal recycle unit. This reactor, invented by de Lasa,<sup>22</sup> overcomes the technical problems of the standard micro-activity test (MAT). The catalytic conversion of cumene is modeled in the present study. The riser simulator consists of two outer shells, a lower section and an upper section, that permit the catalyst to be loaded or unloaded easily. This reactor was designed in such way that an annular space is created between the outer portion of the basket and the inner part of the reactor shell. A metallic gasket seals the two chambers, with an impeller located in the upper section. A packing gland assembly and a cooling jacket surround the shaft supporting the impeller. Upon rotation of the shaft, gas is forced outward from the center of the impeller toward the walls. This creates a lower pressure in the center region of the impeller thus inducing flow of gas upward through the catalyst chamber from the bottom of the reactor annular region where the pressure is slightly higher. The impeller provides a fluidized bed of catalyst particles, as well as intense gas mixing inside the reactor.

The riser simulator operates in conjunction with a series of sampling valves that allow hydrocarbons to be injected and products to be withdrawn following a predetermined sequence in short periods of time. Reaction products are measured by a Hewlett-Packard 5890A GC with a FID detector and an HP-1, 25-m cross-linked methyl silicone capillary column with an outer diameter of 0.22 mm and an internal diameter of 0.33 μm. The coke content is evaluated, with ±4% accuracy, in separate runs. Following this, a sample of coked catalysts is exposed to an oxidizing atmosphere with the CO<sub>2</sub> formed being measured quantitatively. A detailed description of various riser simulator components and the sequence of injection and sampling can be found in Kraemer.<sup>23</sup>

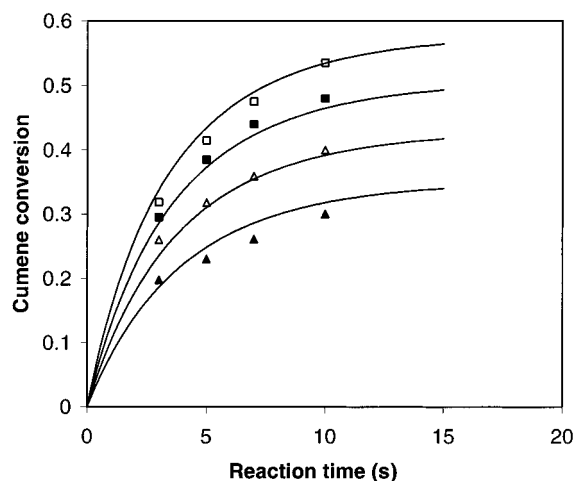
Cumene cracking has been used extensively as a test reaction to investigate the characteristics of any newly developed cracking catalyst.<sup>16</sup> The main reaction pathway of cumene cracking involves the cleavage of the isopropyl group to produce benzene and propene.

## Results and Discussion

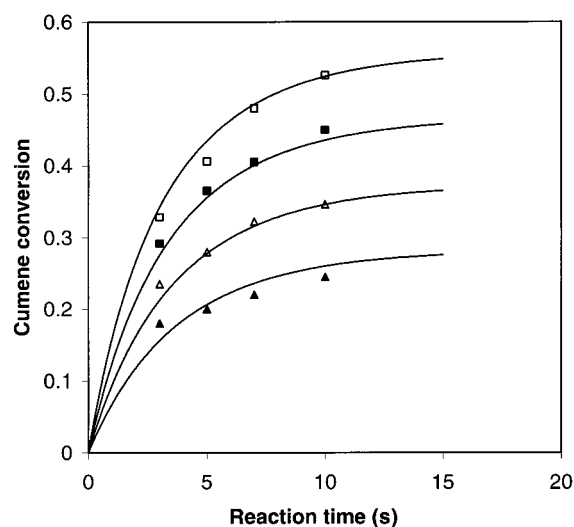
In the present study, two catalysts, CAT-LC (catalyst with large zeolite crystals) and CAT-SC (catalyst with small zeolite crystals), were studied under typical cracking conditions using cumene as the model hydrocarbon reactant molecule. It was observed that the cumene conversion increased with both temperature and reaction time (Figures 1 and 2), with the temperature effect having a mild effect and the reaction time having a relatively more significant influence. For instance, for a 5-s reaction time, the cumene conversions were 23, 32, 38.5, and 41% for temperatures of 400, 450, 500, and 550 °C, respectively. In this respect, the conversion increased 9% from 400 to 450 °C, 6.5% from 450 to 500 °C, and 2.5% from 500 to 550 °C.

Once the decay model based on the time on stream in the context of the riser simulator was established (eq





**Figure 1.** Comparison of experimental and modeling cumene conversions for CAT-LC based on time on stream (eq 10). C/O = 5. Reported experimental points are average values of at least three measurements. Typical errors are  $\pm 2\%$ . (▲) 400, (△) 450, (■) 500, and (□) 550 °C.



**Figure 2.** Comparison of experimental and modeling cumene conversions for CAT-SC based on time on stream (eq 10). C/O = 5. Reported experimental points are average values of at least three measurements. Typical errors are  $\pm 2\%$ . (▲) 400, (△) 450, (■) 500, and (□) 550 °C.

**Table 3. Kinetic Constants for Both CAT-LC and CAT-SC Based on Time on Stream (TOS)**

catalyst	$k_0 \times 10^3$ [m <sup>3</sup> /(kg <sub>cat</sub> s)]	95% CFL	$E_R$ (kJ/mol)	95% CFL	$\alpha$ (s <sup>-1</sup> )	95% CFL	$r^2$
CAT-LC	7.61	1.3	21.35	0.96	0.217	0.066	0.94
CAT-SC	7.24	1.16	27.63	0.89	0.239	0.064	0.96

10), it was tested under a number of operating conditions as follows: (a) four different reaction times (3, 5, 7, and 10 s), (b) four different temperatures (400, 450, 500, and 550 °C), (c) two catalysts prepared with two sizes of zeolite crystals (small crystal CAT-SC and large crystal CAT-LC), and (d) a single catalyst/oil ratio (catalyst/oil = 5).

The three model parameters  $k_0$ ,  $E_R$ , and  $\alpha$  of eq 10 with  $\eta = 1$  were determined using nonlinear regression (MATLAB package). Table 3 reports the parameters obtained and the limited spans for the 95% confidence interval. Tables 4 and 5 (TOS model) report the very low correlations between  $k_0$  and  $E_R$  and  $\alpha$  and the moderate correlation between  $k_0$  and  $\alpha$  for both

**Table 4. Correlation Matrix for CAT-LC (TOS Model)**

	$k_0$	$E_R$	$\alpha$
$k_0$	1	-0.095	0.96
$E_R$	0.095	1	-0.043
$\alpha$	0.96	-0.043	1

**Table 5. Correlation Matrix for CAT-SC (TOS Model)**

	$k_0$	$E_R$	$\alpha$
$k_0$	1	-0.125	0.96
$E_R$	-0.125	1	-0.046
$\alpha$	0.96	-0.046	1

**Table 6. Kinetic Constants for Both CAT-SC and CAT-LC Based on Reactant Conversion (RC)**

catalyst	$k_0 \times 10^3$ [m <sup>3</sup> /(kg <sub>cat</sub> s)]	95% CFL	$E_R$ (kJ/mol)	95% CFL	$\lambda$	95% CFL	$r^2$
CAT-LC	13.0	6.3	52.75	2.88	5.5	1.9	0.94
CAT-SC	14.12	6.62	61.96	3.2	6.2	1.9	0.97

**Table 7. Correlation Matrix for CAT-LC (RC Model)**

	$k_0$	$E_R$	$\lambda$
$k_0$	1	0.73	0.98
$E_R$	0.73	1	-0.75
$\lambda$	-0.98	-0.75	1

**Table 8. Correlation Matrix for CAT-SC (RC Model)**

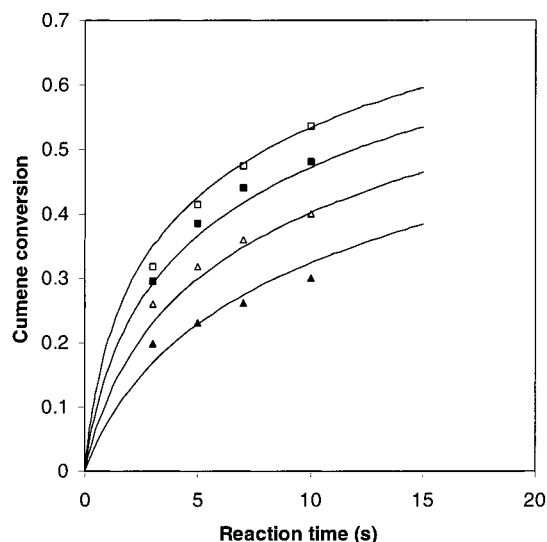
	$k_0$	$E_R$	$\lambda$
$k_0$	1	0.82	0.98
$E_R$	0.82	1	-0.84
$\lambda$	0.98	-0.84	1

CAT-LC and CAT-SC. Figure 1 (CAT-LC) and Figure 2 (CAT-SC) show comparisons of the experimental and model-predicted conversions (eq 10). The adequacy of the model and of the selected fitting parameters is shown in Table 3 given the 0.94–0.97 regression coefficients.

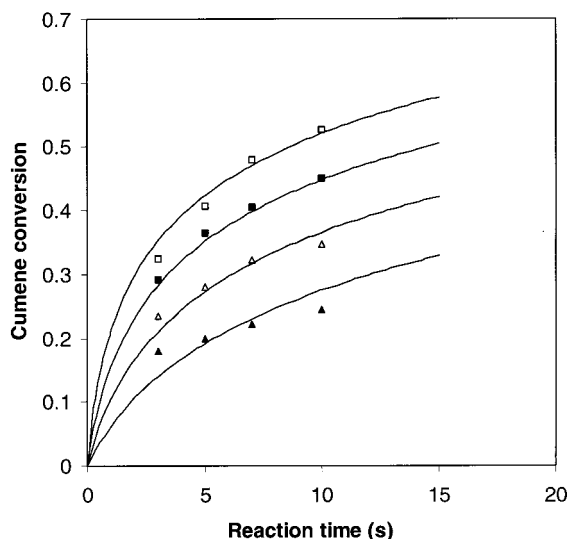
Regarding the kinetic parameters obtained, an interesting result is the consistency of the energy of activation and the activity decay constant, 21.35 and 27.63 kJ/mol and 0.217 and 0.239 s<sup>-1</sup>, respectively, for CAT-LC and CAT-SC. It has to be noticed that these values of  $E_R$  and  $\alpha$  are in the same range as those found by Kraemer<sup>23</sup> for the cracking of alkylaromatics in the riser simulator using a time-on-stream model.

Next, a nonlinear regression involving eq 18, the same experimental data as used with the TOS model, and three adjustable parameters was considered using MATLAB software. Table 6 reports the parameters obtained, and Tables 7 and 8 show low to moderate cross-correlation for the parameters corresponding to CAT-LC and CAT-SC, respectively. Figures 3 and 4 display comparisons of the model results and experimental points for CAT-LC and CAT-SC, respectively. In addition, the adequacy of eq 18 for representing the experimental data is verified by the 0.94–0.97 regression coefficients (Table 6).

It can be observed that the activation energy for cumene cracking based on the reactant conversion (RC) model is in the range of 52.75–61.96 kJ/mol, with these results being in excellent agreement with the 41.8–83.7 kJ/mol activation energies reported for cumene cracking by a large number of researchers, as mentioned in an extensive literature review by Corma and Wojciechowski.<sup>16</sup> In addition, the activity decay constants for both CAT-LC and CAT-SC remain in the small range of 5.5–6.2 (Table 6). Hence, according to this model, at 50% conversion, the catalyst has already



**Figure 3.** Comparison of experimental and modeling cumene conversions for CAT-LC based on reactant converted (eq 18).  $C/O = 5$ . Reported experimental points are average values of at least three measurements. Typical errors are  $\pm 2\%$ . (▲) 400, (△) 450, (■) 500, and (□) 550 °C.



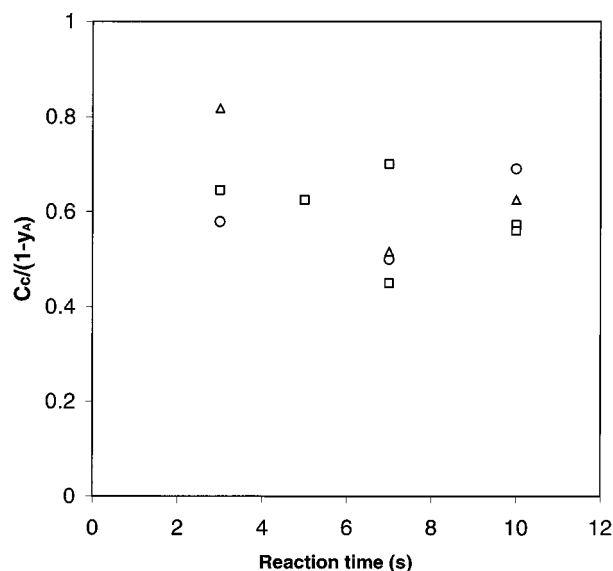
**Figure 4.** Comparison of experimental and modeling cumene conversions for CAT-SC based on reactant converted (eq 18).  $C/O = 5$ . Reported experimental points are average values of at least three measurements. Typical errors are  $\pm 2\%$ . (▲) 400, (△) 450, (■) 500, and (□) 550 °C.

lost 60% of its activity, whereas at 70% conversion, there is a 72% activity loss.

Regarding the activity decay model based on reactant conversion, one main assumption is given by eq 15. This assumption considers  $A$  as a constant parameter that is not affected by cumene conversion

$$A = \frac{C_c}{(1 - y_A)} \quad (19)$$

To check the validity of this assumption, a number of independent runs were performed in which, in addition to the measurement of cumene conversion, the amount of coke formed was determined. On this basis, the quantity  $C_c/(1 - y_A)$  was calculated for each run independently. It was observed that (Figure 5),  $A$  (for CAT-LC) is equal to  $0.6 \pm 0.2$  for the different temperatures and reaction times used in the study. Given that



**Figure 5.** Coke selectivity for cumene conversion as a function of reaction time.  $C/O = 5$ : (△) 400, (○) 500, (□) 550 °C.

the confidence limits for  $A$  are in the  $\pm 15\%$  range, mainly because of the uncertainty in the  $C_c$  measurements, the  $A$  parameter can be assumed constant. This validates the process of numerical integration of eq 18 adopted to calculate  $E_R$ ,  $k_0$ , and  $\lambda$ .

Finally, for CAT-LC, the value of  $\lambda$  determined was 5.5, and using  $A = 0.6$ , one obtains  $\delta = 8.33$ . Thus, eq 16 can also be reported as  $\phi = \exp(-8.33C_c)$ .

It can also be mentioned that  $C_c$  for cumene cracking typically has a value in the range of 0.1–0.2 mass fraction. Then, at  $C_c = 0.15$ ,  $\phi = 0.2866$ , or 71% of the catalyst activity is lost at a 0.15 coke concentration.

Equation 1 includes an effectiveness factor. In both cases, the evaluation of the kinetic parameters assumes that  $\eta = 1$ . This important assumption has to be validated. Toward this end, the modified Thiele modulus ( $h'$ ) for cumene cracking was calculated using eq 7. For instance,  $\alpha$ ,  $k_0$ , and  $E_R$  based on time on stream were set equal to  $0.217 \text{ s}^{-1}$ ,  $0.0076 \text{ m}^3/(\text{kg}_{\text{cat}} \text{ s})$ , and  $23.02 \text{ kJ/mol}$ , respectively (CAT-LC in Table 3). Substituting these parameter values into eq 7 for a reaction temperature of 400 °C and a reaction time of 5 s, the modified Thiele modulus was calculated as 0.095, and the effectiveness factor as 0.996. Similarly, the calculated  $\lambda$ ,  $k_0$ , and  $E_R$  parameters of eq 18 (CAT-LC in Table 6) were used to recalculate the modified Thiele modulus and effectiveness factor. For instance, for a 0.22 cumene conversion, essentially the same  $h'$  and  $\eta$  values, with  $\eta$  very close to unity, were obtained.

It can thus be concluded that cumene cracking in FCC catalysts is controlled by the chemical reaction rate, with diffusional transport constraints having a negligible role. This is, by the way, consistent with the 6.8-Å estimated cumene critical diameter being smaller than the 7.4-Å faujasite zeolite openings.<sup>24</sup>

In summary, the decay models considered in the present study based on cumene conversion and time on stream prove to be adequate for predicting cumene conversions over a rather large range of conversions, temperatures, and reaction times. However, the decay model based on reactant conversion should be preferred given its sounder mechanistic basis. It should also be stressed that the decay model based on reactant conversion was considered under cracking conditions free of

transport constraints and, in this context, the derived decay function can be considered an "intrinsic" activity decay function.

## Conclusions

The catalytic cracking of cumene as a model compound allows FCC catalysts to be tested under conditions free of intracrystalline diffusional constraints with the effectiveness factor remaining very close to unity.

Experiments were developed in a novel riser simulator using two sizes of faujasite crystals (0.4 and 0.9  $\mu\text{m}$ ). The study was conducted under relevant reaction conditions for FCC in terms of temperature, contact time, reactant partial pressure, and catalyst/oil ratio.

A new catalytic activity decay model based on reactant conversion was proposed and tested. This phenomenologically based model is most valuable given that it allows for changes of chemical species to be defined without the specific extra requirement of measuring the coke concentration.

Kinetic and activity decay parameters were estimated for this model using regression analysis, along with their respective confidence intervals. The consistency of the kinetic parameters for the two zeolite crystals is an encouraging result to support the validity of the proposed model.

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## Notation

$A$  = group of parameters, see eq 15  
 $a_{\text{ext}}$  = external surface area (1/m)  
 $B$  = parameter of catalyst activity model, see ref 14  
 $C_A$  = gas-phase concentration of cumene ( $\text{kmol}/\text{m}^3$ )  
 $C_c$  = coke mass fraction ( $\text{kg}_{\text{coke}}/\text{kg}_{\text{cat}}$ )  
 $C_{\text{go}}$  = gas oil concentration ( $\text{kmol}/\text{m}^3$ )  
 $D_{\text{eff}}$  = effective diffusivity ( $\text{m}^2/\text{s}$ )  
 $D_0$  = preexponential constant involved in the definition of the diffusivity coefficient ( $\text{m}^2/\text{s}$ )  
 $E_D$  = activation energy for cumene diffusion ( $\text{kJ}/\text{mol}$ )  
 $E_R$  = activation energy for cumene cracking ( $\text{kJ}/\text{mol}$ )  
 $F$  = parameter catalyst activity decay model, see ref 15  
 $G$  = parameter of the catalyst activity decay model, see ref 15  
 $k_d$  = deactivation rate constant ( $\text{s}^{-1}$ ), see ref 8  
 $k_{d1}$  = deactivation rate constant ( $\text{s}^{-1}$ ), see ref 8  
 $k_{\text{in}}$  = intrinsic kinetic constant for cumene cracking [ $\text{m}^3/(\text{kg}_{\text{cat}} \text{ s})$ ], units based on a first-order reaction  
 $k_{\text{md}}$  = deactivation rate constant ( $\text{s}^{-1}$ ), see ref 16  
 $k_0$  = preexponential factor in Arrhenius equation [ $\text{m}^3/(\text{kg}_{\text{cat}} \text{ s})$ ], units based on a first-order reaction  
 $K_0$  = preexponential factor in Arrhenius equation defined at an average temperature [ $\text{m}^3/(\text{kg}_{\text{cat}} \text{ s})$ ], units based on a first-order reaction  
 $L$  = zeolite crystal size ( $\mu\text{m}$ )  
 $h'$  = modified Thiele modulus, refer to eqs 6 and 7  
 $\text{MW}_A$  = molecular weight of cumene ( $\text{kg}/\text{kmol}$ )

$\text{MW}_c$  = molecular weight of coke ( $\text{kg}/\text{kmol}$ ), set to 800  $\text{kg}/\text{kmol}$

$n$  = reaction order or number of sites involved in the deactivation event

$N$  = parameter decay model, see ref 9

$R$  = universal gas constant [ $\text{kJ}/(\text{kmol K})$ ]

$r_c$  = rate of coke formation [ $\text{kmol}_{\text{coke}}/(\text{kg}_{\text{cat}} \text{ s})$ ]

$r_c^0$  = rate of coke formation excluding catalyst decay [ $\text{kmol}_{\text{coke}}/(\text{kg}_{\text{cat}} \text{ s})$ ]

$r^2$  = regression coefficient

$t$  = reaction time (s)

$T$  = reaction temperature (K)

$T_0$  = average temperature for the experiments of 475 °C or 748 K

$V$  = riser simulator volume ( $45 \times 10^{-6} \text{ m}^3$ )

$W_c$  = catalyst mass (kg)

$W_{\text{hc}}$  = mass of hydrocarbon injected into the riser simulator (kg)

$y_A$  = mass fraction of cumene ( $\text{kg}_{\text{cumene}}/\text{kg}_{\text{hydrocarbons}}$ )

## Greek Symbols

$\alpha$  = deactivation constant for TOS model ( $\text{s}^{-1}$ )

$\delta$  = constant related to coke formation, catalyst decay function based on reactant conversion (RC) model

$\eta$  = effectiveness factor for cumene cracking

$\varphi$  = apparent deactivation function

$\varphi_{\text{in}}$  = intrinsic deactivation function

$\varphi_R$  = residual activity

$\nu_c$  = stoichiometric number for coke [ $\text{kmol}$  of coke/ $\text{kmol}$  of cumene converted]

$\rho_c$  = zeolite crystal density ( $\text{kg}/\text{m}^3$ )

## Abbreviations

CAT-IC = catalyst manufactured with large zeolite crystals (refer to Table 2)

CAT-SC = catalyst manufactured with small crystals (refer to Table 2)

CFL = confidence limit

C/O = catalyst-to-reactant ratio [ $(\text{kg}$  of catalyst)/ $(\text{kg}$  of reactant fed)]

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