Continuous-Mixture Kinetics of Coke Formation from Olefinic Oligomers

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A model for interpreting the molecular-weight distributions is presented for the olefinic oligomers and aromatic coke compounds that are experimentally observed in a catalyzed hexene isomerization process (the primary reaction). Reaction rate expressions for the secondary generation of hexene dimers, trimers and tetramers by irreversible reaction are represented in mass balances for a stirred-tank reactor. Dehydrogenation of the oligomers to form coke aromatics and their subsequent adsorption and desorption are included. A molecular-weight moment method allows solution of the model and computation of time dependence of molecular-weight distributions for all components. The model is consistent with observations of decreased catalyst deactivation rates when coke desorption rates approach coke production rates. Catalyst activity maintenance, which can occur under supercritical conditions, is also predicted by the model.

Introduction

Catalyst deactivation by coke deposition, a problem that continues to challenge the chemical process industries, requires further study to address the issue in innovative ways. Supercritical reaction conditions have been explored for the *in situ* extraction of coke-forming compounds from porous catalysts (Tiltscher et al., 1981; Tiltscher and Hofmann, 1987; Saim and Subramaniam, 1990; Manos and Hofmann, 1991; Adschiri et al., 1991). Extracting the coke-forming compounds from the catalyst surface inhibits dehydrogenation and formation of aromatic coke compounds. This mitigates coke buildup in the pores and therefore slows catalyst deactivation. More recently, Ginosar and Subramaniam (1995) suggested that near-critical reaction mixtures offer an optimum combination of solvent and transport properties for minimizing catalyst deactivation rates by coking. For the Pt/γAl_2O_3-catalyzed isomerization of 1-hexene, Ginosar and Subramaniam (1993) observed that hexene oligomers formed by secondary reactions in the bulk fluid phase are dominant coke precursors. The oligomers, constituting less than 2 wt. % of the reaction mixture, are well known to form aromatic coke species on reforming catalysts such as Pt/γAl_2O_3. In subcritical gas-like reaction mixtures, the aromatic coke species remain strongly adsorbed causing catalyst deactivation with time. The increased desorption of the coke compounds in supercritical reaction mixtures, however, can result in activity enhancement.

To explain the activity maintenance or decay of the catalyst, Subramaniam and McCoy (1994) developed a quantitative interpretation based on a lumped kinetic model for the formation, adsorption, and desorption of coke compounds. The model described the production of hexene oligomers (up to tetramers) in the bulk fluid phase followed by their transformation to coke, that is, polynuclear aromatic compounds (up to tetranuclear compounds). For a continuous-flow stirred-tank reactor (CSTR), the model predicted a gradual decay of catalyst activity leading to total deactivation by coke adsorption when the rate of coke production exceeded the net rate of desorption (at subcritical conditions). At supercritical conditions, the desorption rate was large enough to balance the rates of coke production and adsorption, resulting in a steady-state maintenance of catalyst activity.

The experimental data of Ginosar (1994) demonstrate that the olefins and aromatics constitute mixtures that span molecular-weight (MW) ranges. Figure 1 provides representative GC-FID chromatograms of samples obtained at various times

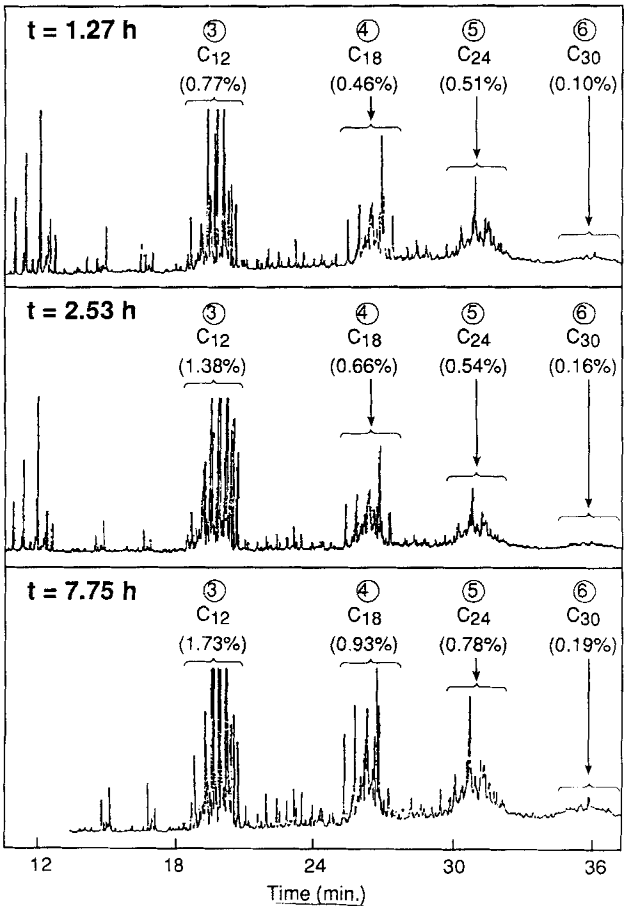

Figure 1. Experimental distributions of oligomers and aromatics determined by GC-MS for the Pt/γAl_2O_3-catalyzed isomerization of 1-hexene at 281°C and 277 bar.

during the run at 281°C and 277 bar, corresponding to a liquid-like reaction mixture density of nearly 0.5 g/cm^3. Four bands (3, 4, 5, and 6) of heavy hydrocarbon compounds elute at 19.8–21.5, 26.2–28.3, 31.2–32.8 and 35.0–37.7 min, respectively. GC-MS analysis indicates that compounds with retention times similar to the four bands have MWs of 168, 252, 336, and 420 amu. These mass units correspond to the MWs expected for the hexene dimer, trimer, tetramer, and pentamer, respectively. The area percentages shown for bands 3, 4, 5, and 6 represent all compounds in the respective C12, C18, C24 and C30 bands. The concentrations of the C12, C18 and C24 components increase with process time, and eventually reach steady values less than 2 wt. %. While the hexene oligomers and their isomers are the dominant species, GC-MS analysis indicated the presence of other compounds such as octene isomers, C10 olefins, and C12 diolefins. In the absence of experimental evidence for disproportionation reactions, the observed molecular-weight distributions (MWDs) in the product mixture are attributed to oligomerization of impurities in the 1-hexene feed (roughly 0.3 wt. % consisting of other olefins in the C3–C8 range). The presence of aromatic species in the reaction mixture was confirmed by HPLC analysis.

This article develops a model for the MWDs of oligomers and coke compounds observed during the coking of a reforming catalyst. The primary reaction is 1-hexene isomerization; the hexene oligomers are *secondary* byproducts formed in relatively low yields (less than 2 wt. %). An example where oligomer formation is the *primary* reaction is the conversion of light olefins to higher molecular-weight olefins on a ZSM-5 catalyst for the production of gasoline and distillate fuels (Quann and Krambeck, 1991; Quann et al., 1988; Tabak et al., 1986). The oligomerization of two olefins of molecular weight x and y yields an oligomer of molecular weight $x+y$. The oligomer in turn serves as a reactant for a further oligomerization. Thus when propylene (C3) is the feed the product sequence is C3, C6, C9, C12, and so on; for hexene as the feed the products are C6, C12, C18, C24, and so on. Quann and Krambeck (1991) and Quann et al. (1988) point out that interfering reactions, such as disproportionation, cracking, and conjunct polymerization, can complicate the reaction pathways and yield intermediate products. Krambeck (1991a) and Quann and Krambeck (1991) proposed a kinetic model for the oligomerization process consisting of a sequence of reversible reactions between olefins. McCoy's (1993) model also treated reversible oligomerization. Formation of aromatic coking compounds and their adsorption and desorption on the catalyst were not included in these models. Krambeck (1991b) provided a conceptual introduction to continuous-mixture oligomerization and catalyst coking.

This article utilizes concepts of continuous-mixture kinetics to describe the production of distributed oligomers from a feed olefin with impurities. The complex mixtures are treated as though MW (or carbon number) is a continuous variable. The hexene feed is approximated as having a MWD ranging from C3 to C8 with most of the distribution in the C6 range. The initial condition (and the feed) for the oligomerization reaction is thus a MWD rather than a single species as approximated by Subramaniam and McCoy (1994). Since the feed is represented by a MWD, the product compounds (oligomers and coke compounds) likewise form MWDs. The oligomers react further to form adsorbed coke compounds, which desorb reversibly. The proposed reversible adsorption-desorption and irreversible reaction rate expressions, in general, have rate coefficients that depend on MW, but may be considered independent of MW for narrow MWDs. The continuous-mixture mass balance equations for a CSTR reduce to the lumped (averaged) equations used by Subramaniam and McCoy (1994) when integrated over the MW.

Coupled nonlinear, ordinary differential equations for the MW moments (integrals over the MWD) are developed and solved easily by numerical solution. The moment procedure is similar to that of McCoy (1993), who applied the moment method to reversible oligomerization kinetics and equilibrium. The moment equations form a hierarchy of increasing detail and information as higher moments are considered. The lumped description (zero moments only) provides the minimum information needed to interpret experimental observations. The MWDs for reactants and products are approximated as Gaussian distributions are constructed from the moments. For the CSTR fed with a narrow distribution of reactant olefins (hexene with C3–C8 inpurities), these MWDs are shown to approach a steady state as time evolves. Although it is possible to present this same kinetic scheme as many discrete reaction steps, the continuous-mixture approach allows efficient construction of governing equations and straightforward solution by MW moment analysis.

Theory

The dominant reaction in the experiments of Ginosar and Subramaniam (1995) is the isomerization of 1-hexene to form cis- and trans-isomers. This primary reaction is two to three orders of magnitude faster than the secondary oligomer and coke formation reactions. The concentration of the isomers in the reaction mixture may thus be considered to be in pseudo-steady state. The same representation proposed by Subramaniam and McCoy (1994) is suitable here; for the reaction:

$$n\text{-}C_6 \rightarrow i\text{-}C_6 \tag{1}$$

the mass balance is

$$(nC_6)_f - (nC_6) = ak_M\tau(nC_6) \tag{2}$$

where $a(t)$ is the catalyst activity (defined below), and τ is the average CSTR residence time. The secondary olefinic oligomerizations and the coke formation reactions are independent of the primary reaction at pseudo steady state. It follows that other primary reactions could be proposed that would allow secondary coking reactions of similar type.

Consider that isomers of component P_1 combine to form the oligomers P_2, which further react to form P_3 and P_4. The oligomers are transformed by dehydrogenation to the adsorbed coke compounds, S_j, $j=2$, 3, 4. The coke can desorb in a reversible manner to form the fluid product compounds, R_j. The MW of P_i will be, on average, i times the MW of P_1. The rate coefficients for the reaction and adsorption-desorption processes are shown in the following reaction pathway scheme:

$$(n\text{-}C_6) \xrightarrow{ak_M} (i\text{-}C_6)$$

$$P_1 + P_1 \xrightarrow{k_{11}} P_2\ (\text{dimer}) \xrightarrow{ak_2} S_2 \underset{k_{a2}}{\overset{k_{d2}}{\rightleftarrows}} R_2$$

$$P_1 + P_2 \xrightarrow{k_{12}} P_3\ (\text{trimer}) \xrightarrow{ak_3} S_3 \underset{k_{a3}}{\overset{k_{d3}}{\rightleftarrows}} R_3$$

$$\left.\begin{array}{ll} P_2 + P_2 & k_{22} \\ P_1 + P_3 & k_{13} \end{array}\right\rangle P_4\ (\text{tetramer}) \xrightarrow{ak_4} S_4 \underset{k_{a4}}{\overset{k_{d4}}{\rightleftarrows}} R_4 \tag{3}$$

The possibility of extending the system to higher MW oligomers is obvious.

Each of the chemical components is considered to comprise a continuous mixture spanning a molecular-weight range. If x is the molecular weight, then for a CSTR model, the MWD for each component is a function of both x and t: $P_i(x, t)$, $S_j(x, t)$, $R_j(x, t)$. The concentration in the range $(x, x+dx)$ is, for example, $P_1(x, t)dx$. The integral over all x for each of these MWDs is the total concentration (zero-order moment).

The ratio of the desorption and adsorption rate coefficients is the desorption equilibrium coefficient:

$$K_j(x) = k_{dj}(x)/k_{aj}(x) = [R_j/A_c w_c S_j]_{\text{equil}} \tag{4}$$

In general all the rate coefficients may be functions of MW.

The reaction rate expressions for the loss and generation of oligomers are similar to the particle agglomeration rate term (Hulbert and Katz, 1964; Himmelblau and Bischoff, 1968). The difference is that here two different chemical species are involved rather than indistinguishable agglomerating particles (McCoy, 1993). This requires separate rate expressions for the consumption and production terms. The rate expressions for the loss of P_1, P_2, and P_3 are, respectively:

$$r_1^{\text{loss}}(x,t) = 2k_{11}(x)P_1(x,t)\int_0^\infty P_1(x',t)dx' + k_{12}(x)P_1(x,t)\int_0^\infty P_2(x',t)dx' + k_{13}(x)P_1(x,t)\int_0^\infty P_3(x',t)dx' \tag{5}$$

$$r_2^{\text{loss}}(x,t) = k_{12}(x)P_2(x,t)\int_0^\infty P_1(x',t)dx' + 2k_{22}(x)P_2(x,t)\int_0^\infty P_2(x',t)dx' \tag{6}$$

$$r_3^{\text{loss}}(x,t) = k_{13}(x)P_3(x,t)\int_0^\infty P_1(x',t)dx' \tag{7}$$

The generation terms for $P_2(x)$, $P_3(x)$, and $P_4(x)$ are, respectively:

$$r_2^{\text{gen}}(x,t) = \int_0^x k_{11}(x')P_1(x-x',t)P_1(x',t)dx' \tag{8}$$

$$r_3^{\text{gen}}(x,t) = \int_0^x k_{12}(x')P_1(x-x',t)P_2(x',t)dx' \tag{9}$$

$$r_4^{\text{gen}}(x,t) = \int_0^x k_{22}(x')P_2(x-x',t)P_2(x',t)dx' + \int_0^x k_{13}(x')P_1(x-x',t)P_3(x',t)dx' \tag{10}$$

As in Subramaniam and McCoy (1994), mass-transfer resistances are ignored. But regardless of transport considerations, the proposed kinetic scheme is needed to describe the multitude of coke precursors and coke compounds that have been observed. Disproportionation, cracking and conjunct polymerization (Quann and Krambeck, 1991; Quann et al., 1988), ignored here, can further contribute to distributing the oligomers. The mass balance equations are written in terms of the feed MWD, $P_{1f}(x)$, and the CSTR average residence time, τ,

$$dP_1/dt = [P_{1f} - P_1]/\tau - r_1^{\text{loss}} \tag{11}$$

$$dP_2/dt = -P_2/\tau + r_2^{\text{gen}} - r_2^{\text{loss}} - ak_2P_2 \tag{12}$$

$$dP_3/dt = -P_3/\tau + r_3^{\text{gen}} - r_3^{\text{loss}} - ak_3P_3 \tag{13}$$

Table 1. Values of the Dimensionless Parameters Used in the Calculations

α_M	0.91	β_2	0.25
α_{11}	1.44 (10^{-3})	β_3	0.52
α_{12}	0.451	β_4	1.1
$\alpha_{13}=\alpha_{22}$	0.188	$\gamma_2=\gamma_3=\gamma_4$	0.01
		ϕ	2,060.

$$dP_4/dt = -P_4/\tau + r_4^{\text{gen}} \qquad -ak_4P_4 \tag{14}$$

$$A_cw_cdS_j/dt = k_{ja}R_j - A_cw_ck_{jd}S_j + ak_jP_j \qquad j=2,3,4 \tag{15}$$

$$dR_j/dt = -k_{ja}R_j + A_cw_ck_{jd}S_j - R_j/\tau \qquad j=2,3,4 \tag{16}$$

The initial conditions allow for an initial charge of P_1:

$$P_1(x,t=0) = P_{1o}(x) \tag{17}$$

$$P_j(x,t=0) = 0 \qquad j=2,3,4 \tag{18}$$

$$S_j(x,t=0) = 0 \qquad j=2,3,4 \tag{19}$$

$$R_j(x,t=0) = 0. \qquad j=2,3,4 \tag{20}$$

In the calculations that follow, the feed and initial MWDs are identical: $P_{1f}(x) = P_{1o}(x)$. Aside from the introduction of the MW dependence, the governing differential equations follow the lumped reaction scheme proposed by Subramaniam and McCoy (1994). The oligomerization reactions are identical to the fusion reactions in the reversible oligomerization system of McCoy (1993).

The molecular-weight moments of the MWDs are defined as:

$$Y_i^{(n)}(t) = \int_0^\infty x^n Y_i(x,t)dx \tag{21}$$

where Y_i is P_i, R_j or S_j. The zero-order moments ($n=0$) are simply the time-dependent lumped concentrations of the different species. The normalized first moment (average MW) and the second central moment (variance of the MWD) are given, respectively, by:

$$Y_i^{\text{avg}} = Y_i^{(1)}/Y_i^{(0)} \tag{22}$$

and

$$Y_i^{\text{var}} = Y_i^{(2)}/Y_i^{(0)} - [Y_i^{\text{avg}}]^2 \tag{23}$$

The Gaussian representation for the MWD can be written in terms of the MW moments:

$$Y_i(x,t) = [Y_i^{(0)}/(2\pi Y_i^{\text{var}})^{1/2}] \exp[-(x - Y_i^{\text{avg}})^2/2Y_i^{\text{var}}] \tag{24}$$

The catalytic activity is defined in terms of the total amount of adsorbed coke:

$$a(t) = 1 - (1/W_s)\Sigma S_i^{(0)}(t) \tag{25}$$

where W_s is the concentration of coke on the catalyst at total deactivation. Representations of activity a as other than linear (such as exponential) in $S_i^{(0)}$ are easily implemented.

We define scaled quantities to conform to the dimensionless nomenclature of Subramaniam and McCoy (1994):

$$u_i = P_i/P_{if}^{(0)}, \quad r_i = R_i/P_{if}^{(0)}, \quad s_i = S_i/W_s,$$

$$\theta = t/\tau, \quad \alpha_M = k_M\tau, \quad \alpha_{ij} = k_{ij}\tau P_{if}^{(0)},$$

$$\beta_i = k_i\tau, \quad \gamma_i = k_{ai}\tau, \quad \phi = P_{1f}^{(0)}/W_sA_cw_c. \tag{26}$$

The values of the dimensionless parameters used in the calculations are listed in Table 1. The space velocity was 135 g hexene/g cat/h, and the residence time, τ, based on the CSTR volume was 1.4 h.

Since Ginosar (1994) found that the MWDs for the coke groups spanned a narrow range of molecular weights, a reasonable assumption is that the rate coefficients are independent of x. To obtain differential equations for the moments, we multiply the CSTR mass balance equations by $x^n dx$ and integrate. The binomial coefficient, $\binom{n}{r} = n!/(n-r)!r!$, arises due to the substitution of an integration variable, $y = x - x'$, in the expressions for r^{gen} and the subsequent expansion of $(y + x')^n$. The general, nth-order moment equations take the form:

$$du_1^{(n)}/d\theta = u_{1f}^{(n)} - u_1^{(n)} - 2\alpha_{11}u_1^{(n)}u_1^{(0)} - \alpha_{12}u_1^{(n)}u_2^{(0)} - \alpha_{13}u_1^{(n)}u_3^{(0)} \tag{27}$$

$$du_2^{(n)}/d\theta = u_2^{(n)} - \alpha_{12}u_2^{(n)}u_1^{(0)} - 2\alpha_{22}u_2^{(n)}u_2^{(0)} + \alpha_{11}\Sigma\binom{n}{i}u_1^{(n-i)}u_1^{(i)} - a\beta_2u_2^{(n)} \tag{28}$$

$$du_3^{(n)}/d\theta = u_3^{(n)} - \alpha_{13}u_3^{(n)}u_1^{(0)} + \alpha_{12}\Sigma\binom{n}{i}u_1^{(n-i)}u_2^{(i)} - a\beta_3u_3^{(n)} \tag{29}$$

$$du_4^{(n)}/d\theta = u_4^{(n)} + \alpha_{22}\Sigma\binom{n}{i}u_2^{(n-i)}u_2^{(i)} + \alpha_{13}\Sigma\binom{n}{i}u_1^{(n-i)}u_3^{(i)} - a\beta_4u_4^{(n)} \tag{30}$$

$$ds_j^{(n)}/d\theta = \gamma_j\phi r_j^{(n)} - \gamma_jK_js_j^{(n)} + a\phi\beta_ju_j^{(n)} \qquad j=2,3,4 \tag{31}$$

$$dr_j^{(n)}/d\theta = (1-\gamma_j)r_j^{(n)} + (K_j\gamma_j/\phi)s_j^{(n)} \qquad j=2,3,4 \tag{32}$$

For $n=0$ we obtain ten zero-moment equations. As the zero moment is the concentration of each species, these equations are identical to the mass balance equations used by Subramaniam and McCoy (1994). Additionally, there are ten first-moment equations ($n=1$) and ten second-moment equations ($n=2$). The resulting 30 coupled nonlinear, differential equations are solved by a fourth-order Runge-Kutta routine with variable-step adjustment. The moment equations form a sequential hierarchy since the zero moment equations can be solved independently. Those results are used to solve the first moment equations, and those in turn are used to solve the second moment equations. In the moment equations the catalyst activity varies with time, $a(t)$, and is updated at each time step of the numerical integration.

Results

The 30 differential equations for the moments of P_i, S_j, and

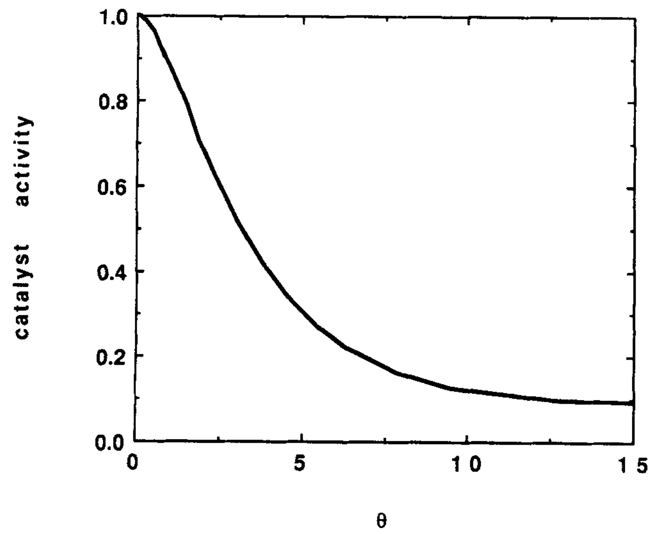

Figure 2. Catalyst activity history showing activity maintenance at steady state for the CSTR model.

R_j provide the information needed to construct the MWDs of all the species in the reactor. The rate coefficients and other parameters, identical to those of Subramaniam and McCoy (1994), are presented in Table 1.

The initial MWD is identical to that of the hexene feed (MW = 84) entering the CSTR with variance $20 = 7{,}076 - 84^2$, that is:

$$u_1^{(0)}(t=0) = u_{1f}^{(0)} = 1$$
$$u_1^{(1)}(t=0) = u_{1f}^{(1)} = 84$$
$$u_1^{(2)}(t=0) = u_{1f}^{(2)} = 7{,}076 \qquad (33)$$

The feed MWD, with characteristic width $\sqrt{20}$, is thus a relatively narrow distribution in MW. Representing the MWD as a Gaussian (normal density) function allows an estimation of mass fractions within certain ranges of MW (Feller, 1965).

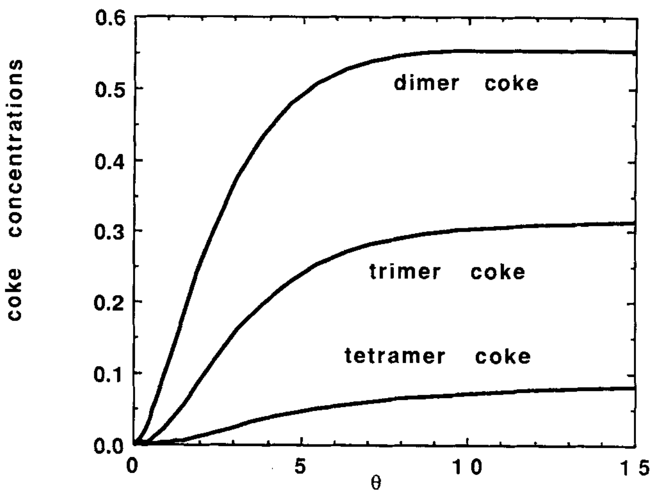

Figure 4. Fractional coke coverage (scaled zero moments of MWDs for dimer, trimer, and tetramer coke) vs. time.

Since the root of the variance is 4.5, then 68.3% of the mass is in the range of MW 84 ± 4.5, 95.6% is in the range 84 ± 2(4.5), and 99.7% is in the range 84 ± 3(4.5). As the MWs of pentene, hexene, and heptene are 70, 84, and 98, we see that about 0.3% of the feed corresponds to pentene and heptene (and other) impurities. This agrees well with the fraction of impurities in hexene feed measured by Ginosar (1994).

The results are presented as the evolution of the zero moments and the MWDs with time in Figures 2-8. The zero moments are simply the mass concentrations of the species in each MW range or lump. These quantities, and hence the catalyst activity, echo the results presented by Subramaniam and McCoy (1994). Figure 2 shows how the catalyst activity declines to a constant value after about 10 residence times when coke desorption rates balance coke production rates. This case of catalyst activity maintenance allows the main reaction, 1-hexene isomerization, to continue indefinitely in the CSTR. The oligomer concentrations, zero moments of $u_i(x, t)$, i

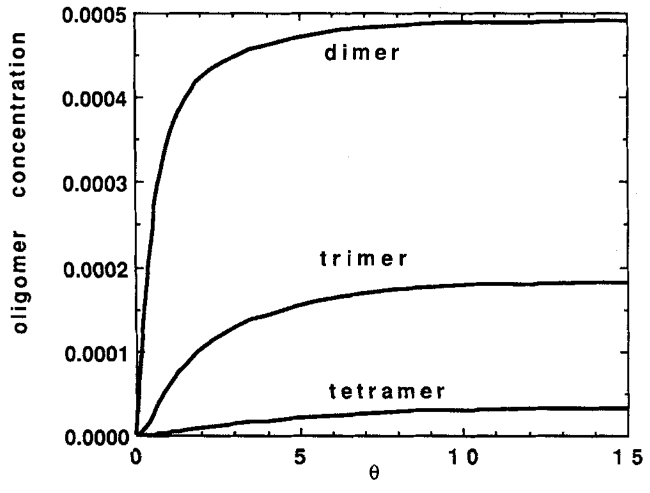

Figure 3. Oligomer concentrations (scaled zero moments of MWDs for dimer, trimer, and tetramer) vs. time.

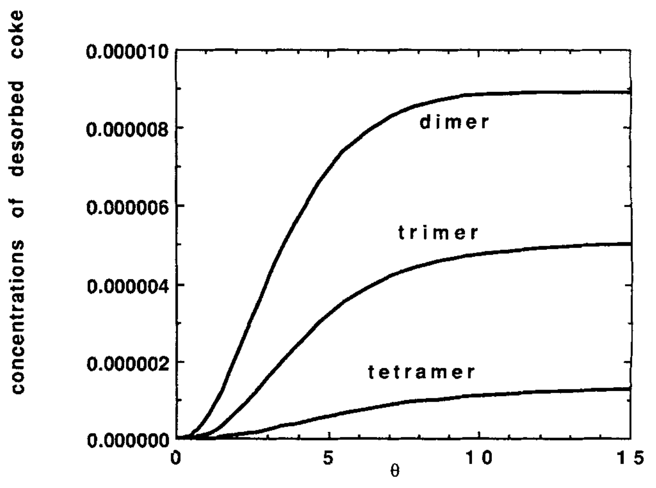

Figure 5. Desorbed coke concentrations (scaled zero moments of MWDs for desorbed dimer, trimer, and tetramer coke) vs. time.

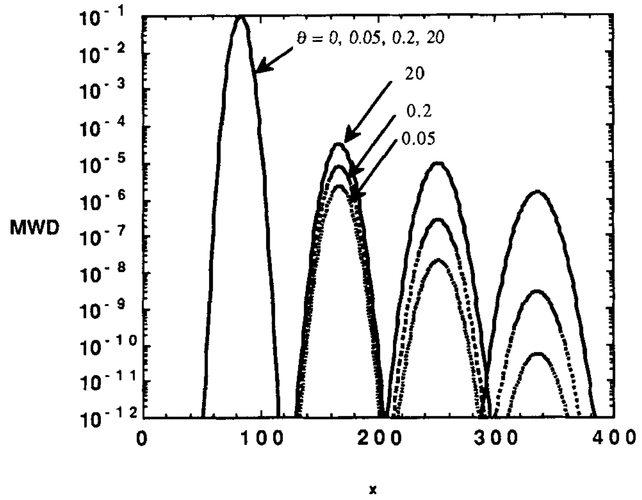

Figure 6. Calculated MWDs for hexene and its oligomers.

= 1,2,3,4, are displayed in Figure 3 as a function of time. Coke coverages on the surface and desorbed coke concentrations, zero moments of $s_j(x)$ and $r_j(x)$, are shown in Figures 4 and 5, respectively.

For the feed and initial conditions considered, the values of the average and the variance of all the MWDs are constant with time, that is:

$$Y_j^{\mathrm{avg}}(t) = 84j$$

and

$$Y_j^{\mathrm{var}}(t) = 20j, \quad j = 1,2,3,4 \tag{34}$$

This time-independent behavior can be verified, for example, by setting up the expression:

$$dY_j^{\mathrm{avg}}/dt = d[Y_j^{(1)}/dY_j^{(0)}]/dt \tag{35}$$

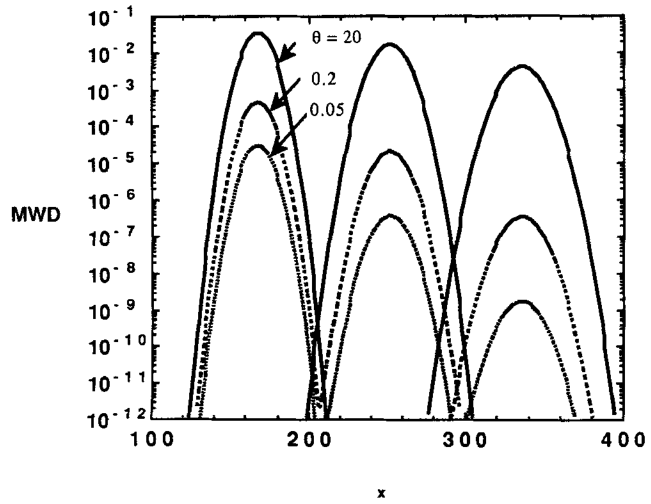

Figure 7. Calculated MWDs for coke compounds (adsorbed aromatics) showing increasing coverages with time.

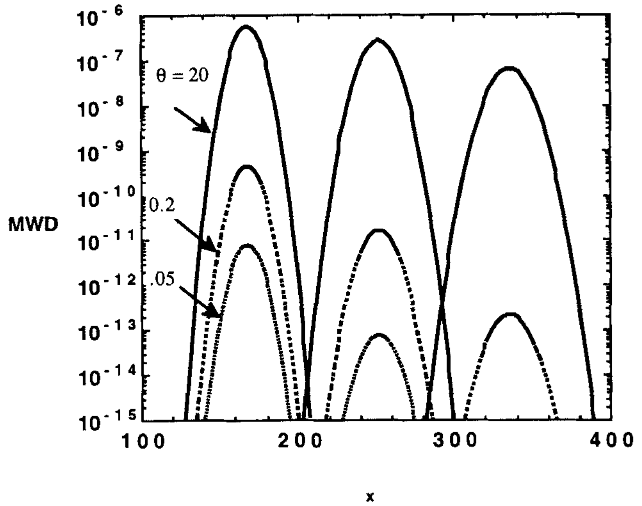

Figure 8. Calculated MWDs for aromatics (desorbed coke compounds) showing increased desorption with time.

and showing by substitution that it equals zero. Such behavior would not be observed when the rate constants depend on x. For narrow peaks, however, taking the k_i and k_{ij} values as constant with x is a reasonable approximation. The variance and average of the product molecules are additive in their reactants. The MWDs for $u_i(x)$, $s_j(x)$, and $r_j(x)$ are provided in Figures 6, 7 and 8. The area under each Gaussian peak is the zero moment, or concentration. In Figure 6, since the amount of dimers, trimers, and tetramers that are formed by the secondary reactions is very small, the MWD for $u_1(x)$ does not change significantly with time. It is evident that the continuous-mixture approach describes the MWDs for the oligomers and coke compounds, indicates their time dependence, and provides therefore a deeper level of understanding of the coking process.

Conclusion

Conventional coking models for subcritical conditions usually employ a single coke formation reaction wherein all the coke compounds are lumped as one irreversibly-adsorbed compound (see, for example, Froment and Bischoff, 1990). Such approximate models may be adequate at subcritical reaction conditions when insignificant desorption of coke occurs. These models, however, can neither predict the mixture of coke compounds observed in the reactor effluent nor can they describe the possibility of catalyst activity maintenance at supercritical reaction conditions. In contrast, the proposed kinetic scheme can predict either catalyst activity maintenance or total activity decay. Moreover, when the higher moments are included in the solution to the governing equations for the MWDs, the kinetic scheme can portray the complex mixtures that are a consequence of impure feed to the reactor.

The continuous-mixture model thus provides a framework for describing the complex multicomponent dynamics of catalytic coking processes. Reactant hexene oligomerizes into dimers, trimers, and tetramers, which subsequently are transformed to coke. The MWDs for the CSTR show the time-dependent formation and evolution of the oligomers and aromatic coke compounds. In addition to oligomerization and aromatization reactions, adsorption-desorption phenomena are described as continuous-mixture rate processes. The governing integro-differential equations for the MWDs are converted to MW moment equations, which are ordinary differential equations that are readily solved for the first three (zero, first, and second) moments. The MWDs are reconstructed as Gaussian distributions from the moments. The model is consistent with reported observations of decreased catalyst deactivation rates when coke desorption rates approach coke production rates. The proposed model predicts the following additional features observed experimentally at supercritical conditions for Pt/γAl_2O_3-catalyzed 1-hexene reaction in a CSTR:

- At supercritical operating conditions, the 1-hexene conversion (or catalyst activity) decays with time. Because *in situ* coke extraction occurs, however, the deactivation rate is slower compared to subcritical conditions (Saim and Subramaniam, 1990).
- At supercritical conditions, hexene oligomers (up to pentamers) are observed among compounds having the MWDs shown in Figure 1. These oligomers, even though present in low concentrations, are dominant coke precursors (Ginosar, 1994).
- Due to the liquid-like densities of supercritical reaction mixtures, coke compounds such as polyaromatic hydrocarbons are extracted from the catalyst and hence appear in the reactor effluent (Subramaniam and Ginosar, 1995).

The proposed model thus leads to a more detailed description of the chemical processes underlying coking of a reforming catalyst in olefinic reaction mixtures.

Notation

a = catalyst activity
A_c = surface area of catalyst, cm^2/g cat
k_j = rate coefficient for catalytic dehydrogenation of oligomers to aromatics, 1/h
k_M = rate coefficient for 1-hexene isomerization on the catalyst, 1/h
K_j = desorption equilibrium coefficient, $j=2, 3, 4$, dimensionless
k_{aj} = adsorption rate coefficient for fluid-phase aromatics, 1/h
k_{dj} = desorption rate coefficient for surface aromatics, 1/h
k_{ij} = rate coefficient for oligomerization, cm^3/h/mol
$P_i(x,t)$ = oligomer MWD in the fluid phase, mol/cm^3
$P_{1f}(x)$ = MWD of P_1 in the feed, mol/cm^3
$P_{1f}^{(0)}$ = zero moment of feed MWD, mol/cm^3
r_j = MWD of aromatics in the fluid phase
$R_j(x,t)$ = desorbed aromatics MWD, mol/cm^3
s_j = MWD of adsorbed coke
$s_j^{(n)}$ = nth moment of s_j
$S_j(x,t)$ = sorbed aromatics (coke) MWD, mol/cm^2
t = time, h
u_i = MWD of oligomers, $i=1,2,3,4$
$u_i^{(n)}$ = nth moment of u_j
w_c = catalyst loading in the reactor, g cat/cm^3
W_s = concentration of coke on catalyst at total deactivation, mol/cm^2
x = molecular property: MW or carbon number

Greek letters

α_{ij} = $k_{ij}P_{1f}\tau$; rate constant for oligomer formation reactions
α_M = $k_M\tau$; rate constant for isomer formation on the catalyst from 1-hexene
β_j = $k_i\tau$; rate constant for aromatics (mobile coke) formation from oligomer P_i
γ_j = $k_{ai}\tau$; rate constant for adsorption of aromatics S_i
θ = t/τ; time
τ = residence time based on CSTR volume, h
ϕ = $P_{1f}/(W_sA_cw_c)$, dimensionless

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