Kinetics of Deactivation of Bifunctional Pt/Al_2O_3-Cl Catalysts by Coking

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The catalytic activity, product selectivity, and coke deposition were studied during methylcyclopentane (MCP) reforming on bifunctional Pt/Al_2O_3-Cl reforming catalysts with different metal loadings, but constant metal dispersion as well as constant Cl loading. Surprisingly, the overall conversion of MCP was found to decrease as the metal content of the catalyst increased. Analysis of the coke by temperature programmed oxidation (TPO) revealed two distinct peaks, one associated with coke on the metallic function and the other associated with coke on the acidic function. The change of activity of the metal and acid functions with time was monitored by following the rates of hydrogenolysis and hydrocracking, respectively. A mechanistically-based dual-site model for the kinetics of coke formation and the resulting deactivation was developed. The model successfully correlates the experimental data and is an improvement over existing models, since it explicitly accounts for the deactivation of both the metal and the acid functions.

Introduction

The catalytic reforming of naphtha, designed to increase its octane number or to produce aromatics, is a process of great commercial importance (Franck and Martino, 1982). The desired reactions occurring during the reforming process include dehydrogenation of cyclohexanes into aromatics, dehydrogenation of alkanes into olefins, ring enlargement of alkylcyclopentanes into cyclohexanes, isomerization of *n*-alkanes into branched alkanes, and dehydrocyclization of *n*-alkanes into aromatics. In addition, some undesirable side reactions such as hydrocracking and hydrogenolysis occur that result in the formation of light products, C_1 to C_4. The reforming process requires the catalyst to be bifunctional, consisting of a metallic function and an acidic function. The metallic function on the reforming catalyst is represented by Pt, or its bimetallic successors containing Re, Ir, Sn or Ge, etc., as the second component, dispersed on a chlorinated alumina support that also provides the acidic function. The metallic component mainly provides hydrogenation-dehydrogenation and hydrogenolysis activity, whereas the chlorinated alumina provides the cracking and isomerization activity. Dehydrocyclization, ring enlargement, and the bifunctional isomerization reactions require the participation of both functions.

Side reactions occurring during reforming also lead to the formation of carbonaceous residue or coke on the surface of the catalyst. This causes a reduction of the activity and selectivity for the desired reforming products and a consequent reduction in the product octane number. In fact, the operating conditions used in the industry for reforming are dictated largely by efforts to reduce coking and its deleterious effects. These include using a high H_2 partial pressure, which is thermodynamically undesirable, and the need to gradually raise the reformer temperature that concomitantly increases the side reactions. In addition, periodic stoppages are necessary for regeneration of the coked catalyst. A useful consequence of coking, however, is a suppression of the hydrogenolytic activity of the virgin catalyst.

Deactivation, due to coke formation, is a complex process that afflicts the majority of organic gas-phase catalytic reactions. A number of different approaches of varying levels of sophistication have been developed to model the deactivation behavior associated with coke formation (Shum et al., 1987; Pacheco and Petersen, 1984; Corella and Asua, 1982; Froment,

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1980; Froment and Bischoff, 1979a; Wolf and Petersen, 1977, Wojciechowski, 1974; Mahoney, 1974; Levenspiel, 1972; Froment and Bischoff, 1961; Voorhies, 1945), starting with the pioneering work of Voorhies (1945), who related the amount of coke formed on the catalyst to the time of reaction. Other empirical approaches directly relate the reduction in catalytic activity to the time on stream or to the amount of coke accumulated on the catalyst surface (Froment and Bischoff, 1979a). More fundamental approaches utilize mechanistically-based kinetic expressions (Corella and Asua, 1982; Froment, 1980; Wolf and Petersen, 1977). Pacheco and Petersen (1984) have proposed a multiplet fouling model to account for the apparent variable reaction order of fouling by assuming a gradual transition in the number of sites involved in the rate-determining step. Most of the modeling schemes, however, are based on the assumption of homogeneous catalytic sites and cannot thus account for the inherent bifunctional nature of the reforming catalyst. This is desirable since temperature-programmed oxidation studies (Parera and Beltramini, 1988a; Mieville, 1986; Barbier et al., 1985) have clearly shown that coke is deposited on *both* of the catalyst functions. More recently, Butt and Petersen (1988) have extended the modeling of deactivation to account for the possible heterogeneity of catalytic sites.

This study explicitly accounts for the coke deposition and the consequential deactivation of both of the catalyst functions during methylcyclopentane (MCP) reforming on Pt/Al_2O_3. MCP was chosen because of its coking propensity (Barbier, 1986; Beltramini, 1983; Cooper, 1980). The metal content of the catalysts was varied, while maintaining a constant dispersion, so that its effect on the catalyst activity and deactivation could be investigated. A dual-site model based on mechanistic considerations was developed for the kinetics of coke formation and the resulting site deactivation. It predicts quite well much of the experimentally observed behavior.

Experimental Study

Catalyst

High-purity γ-alumina powder (30–80 mesh) CK-300 from Cyanamide Ketjen (Amsterdam) with very low Na and Fe content and a specific surface area of 198 $m^2 \cdot g^{-1}$ was used as the support. Pt/Al_2O_3 catalysts with different metal loadings were prepared and characterized as described by Beltramini and Trimm (1987). The metal dispersion, D, was measured using H_2 by the method of Boudart et al. (1966). Knowledge of the dispersion, D, and the fractional Pt loading, ω_M, allowed the calculation of the number of exposed metal atoms per gram of catalyst, M_0, by using the relation, $M_0 = \omega_M DN/A_{wM}$, where N is Avagadro's number and A_{wM} is the atomic weight of platinum. The number of chlorine atoms per gram of catalyst, A_0, representative of the number of strong acid sites, was determined from the chlorine loading, ω_A, by using the relation, $A_0 = \omega_A N/A_{wA}$ where A_{wA} is the atomic weight of chlorine. It should be pointed out that although the introduction of Cl produces strongly acidic sites, the unchlorinated alumina sites also are somewhat acidic. Both of the Brønsted and Lewis acidities are present in the form of surface OH^- and Al^{3+} species, respectively. The acidic strength of the OH^- groups, however, is markedly enhanced by the Cl^- ions. Therefore, we have related the number of acidic sites to the chlorine content of the catalysts. The composition of the catalysts used is given in Table 1. It may be noted that the number of Cl atoms is 5 to 15 times that of exposed Pt atoms.

Table 1. Catalyst Compositions

Pt wt. %	D %	Cl wt. %	$M_0 \times 10^{-19}$ No. of Pt Atoms/g	$A_0 \times 10^{-19}$ No. of Cl Atoms/g
0.50	75	0.90	1.16	15.3
0.75	70	0.87	1.62	14.8
1.00	68	0.88	2.10	14.9
1.25	72	0.92	2.78	15.6

Feed

Pure H_2 and methylcyclopentane (Reidel-De Haen, Prosynth, 99.9% purity) dried over molecular sieve 4A were used.

Apparatus and procedure

Kinetic experiments were conducted in a flow reaction apparatus (Beltramini et al., 1986). Operational conditions for each run were 5 atm, 773 K, WHSV = 2, and a H_2:MCP molar ratio = 4. These conditions were chosen as they are favorable for enhanced coke formation. The run length was typically 6 h. The total conversion and selectivity toward the different products were calculated using the method previously described (Sad et al., 1980). Other details of the operation procedure and GC analysis conditions are described by Beltramini et al. (1986).

A stainless-steel high-pressure microbalance (Sartorious Model 4401) was used under the same operating conditions as those of the kinetic runs to detemine the amount of coke deposited on the catalyst as a function of time. A Temperature-Programmed Oxidation (TPO) Analyzer (DuPont 951) was used to examine the nature of the carbonaceous species adsorbed on the catalyst surface. Fresh catalyst was used as a reference. The heating rate used was $10°C \cdot min^{-1}$, and pure oxygen was utilized at a flow rate of 50 $cm^3 \cdot min^{-1}$. The temperature difference recorded between the coked sample and the reference (Figure 1) is a measure of the rate of heat evo-

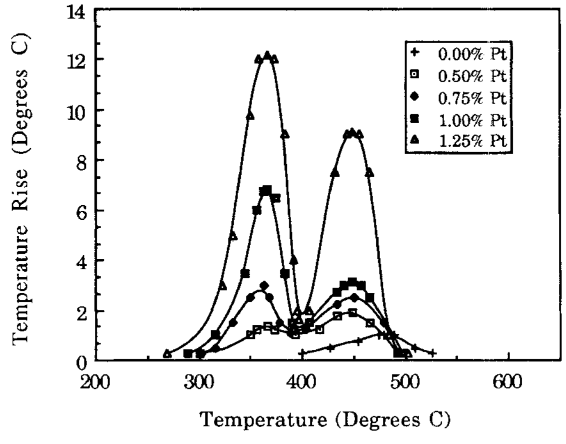


Figure 1. TPO profiles for used catalysts with different Pt loadings.

The first peak is associated with coke deposited on the metal and the second with coke deposited on the support.

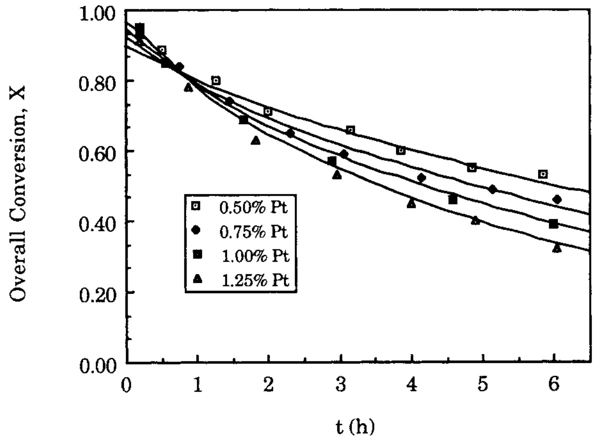


Figure 2. Comparison of model predictions with data for overall MCP conversion vs. time for different Pt loadings.

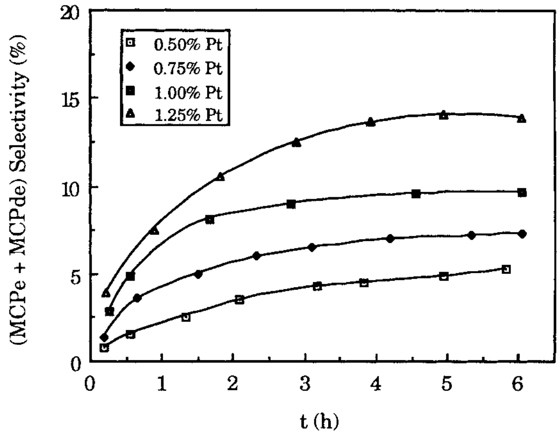


Figure 4. Selectivity for dehydrogenation products (MCPe and MCPde) vs. time for different Pt loadings.

lution as a result of coke combustion. The area under the TPO curve is proportional to the total amount of heat evolved and hence to the amount of coke (Wendlant, 1964). The location of peak temperature is a measure of the chemical nature of the coke species and the site of location.

Experimental results

The overall conversion of MCP as a function of time for different metal loadings, but constant dispersion (Table 1), is given in Figure 2. Initially, each catalyst exhibited a period of rapid deactivation followed by a more gradual decline in the activity. When the conversion vs. time was plotted on a semilog plot (Shum et al., 1987), two distinct slopes were evident at small and at relatively large times. Figure 2 also shows the rather curious and, heretofore, unreported result that, except at rather short times, there is an inverse relationship between conversion and the Pt content. The total amount of coke accumulated on the catalyst as a function of time for the different metal loadings is shown in Figure 3. Coke deposition occurs rapidly at first and then more gradually as time passes, the amount of coke on the catalyst at a given time being greater at higher Pt content. The inverse relationship between conversion and metal loading may, therefore, be qualitatively explained by the fact that there is disproportionately greater amount of coke at higher metal content, likely due to the greater production of the coke precursors, namely methylcyclopentene (MCPe) and methylcyclopentadiene (MCPde), at the higher metal content as shown in Figure 4.

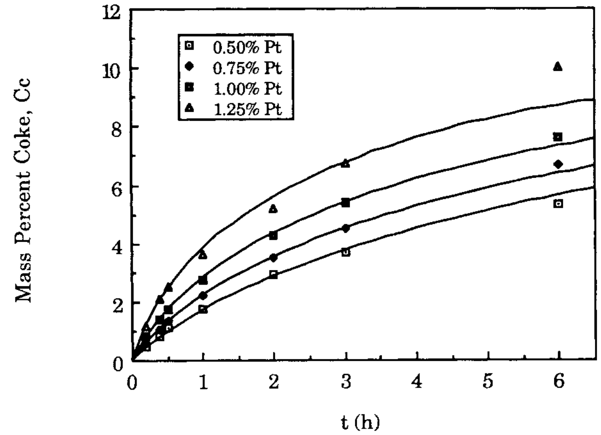


Figure 3. Comparison of model predictions with data for total coke deposition vs. time for different Pt loadings.

The catalyst samples were subjected to temperature-programmed oxidation (TPO) at the end of each run (6 h). The TPO profiles are given in Figure 1 for catalysts with Pt content varying from 0 to 1.25%. Two distinct peaks are seen for all the catalyst samples except for the one without any Pt that produces only the higher temperature peak. It is generally accepted that the lower temperature peak (approximately 370°C) corresponds to coke deposited on, or in contact with, the metal, and the higher temperature peak (approximately 445°C) is due to the coke on the support (Figoli et al., 1983; Barbier et al., 1980). Figure 1 clearly shows that the coke deposition on both functions is enhanced by increased metal content. The amount of coke on the metal phase exhibits a rather steady increase with metal loading (Beltramini and Datta, 1991). Coke deposition on the acidic function exhibits a more nonlinear dependence on the metal content with a dramatic increase occurring between catalysts with Pt content of 1.00 and 1.25%. Barbier (1986) also observed a positive correlation between the metal loading and the extent of coking on the support during conversion of cyclopentane, cyclohexane, and *n*-heptane on Pt/Al_2O_3. Figure 1, hence, appears to lend credence to Barbier's proposition that coke precursors are formed on the metal and then migrate to the support.

The catalytic activity at the beginning of the run was found to be high due in large part to the extensive hydrogenolytic activity (*C-C* bond scission) of the virgin Pt crystallites to primarily produce methane (C_1). As time goes on, however, there is a precipitous decline in the C_1 formation, with the effect being more pronounced at the higher metal loadings (Figure 5). The sharp drop in C_1 selectivity due to coking may be interpreted in terms of a geometric effect. Hydrogenolysis is generally considered to be a "demanding reaction," i.e., an ensemble of two or more contiguous metal atoms is required to form an active site (Gates et al., 1979). Davis et al. (1982)

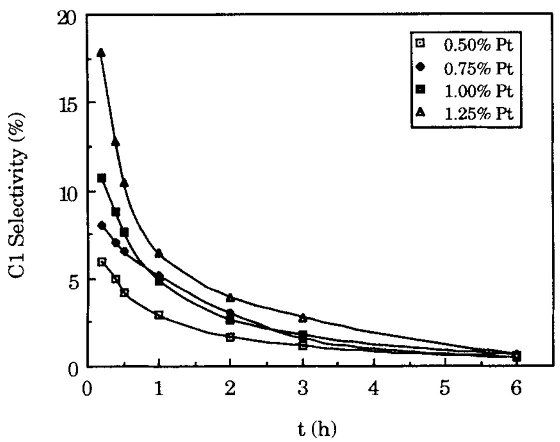


Figure 5. C_1 selectivity data vs. time for different Pt loadings.

have proposed that most of the Pt surface gets covered by coke, and hydrocarbon conversion occurs over the remaining bare metal islands of one or more proximate atoms. As coke deposition on the Pt surface proceeds, the possibility of having ensembles of many contiguous atoms decreases greatly. Thus, coking may be expected to retard hydrogenolysis more severely than a less demanding reaction such as hydrogenation or dehydrogenation.

The selectivity of MCP ring opening occurring at the metallic function can also provide information regarding the size of the Pt ensembles. The products of this reaction are branched pentanes and normal hexane (n-C_6). Parera and Beltramini (1988a) have argued that the ratio of 3-methylpentane (3MP) to n-C_6 is sensitive to the size of the active ensembles with larger ratios corresponding to larger remnants of bare metal. Table 2 shows a substantial decrease in the 3MP/n-C_6 ratio for each catalyst between 0.2 h and 6 h as a result of coke deposition. Moreover, catalysts with higher metal loadings exhibit a somewhat greater reduction in this ratio over the course of the runs. These results appear to corroborate the conclusion from the C_1 activity data that coke deposition on the metal effectively fractionates its surface into progressively smaller bare patches and that this process may be more pronounced at higher metal content.

The nonuniform coking of the metallic and acid functions leads to a change in the distribution of products as shown in terms of the initial (I) (0.2 h) and final (F) (6 h) product selectivities in Table 2. As discussed above, C_1 production is severely suppressed by coking at the metal function. The selectivities for products arising from other metal catalyzed reactions, such as ring opening (iso- and n-C_6) and dehydrogenation (e.g., MCPe and MCPde, Figure 4), in fact, show the opposite trend. Apparently, as the size of active Pt ensembles is reduced, a site may become inactive for hydrogenolysis but may still be active for less demanding reactions such as those cited above. The increase in the selectivities of iso- and n-C_6 and in MCPe and MCPde production, thus, appears to be at the expense of a sharp drop in C_1 selectivity with the coking of metal. Figure 4 also shows that the selectivity for MCPe and MCPde is enhanced by increased metal loading.

The selectivity of hydrocracking products, C_2 - C_5, shows a decrease over the course of the runs. This change is selectivity of products formed by hydrocracking, which occurs primarily on the acid sites by bond rupture via the carbonium ion mechanism (Pines, 1981), with little or no C_1 production (Parera et al., 1983), is indicative of the deactivation of the acid sites. It is seen from Table 2 that hydrocracking selectivity is very high when the metal function is absent. Moreover, catalysts with progressively higher Pt content exhibit decreasing $C_2 - C_5$ selectivity. This is consistent with the TPO results (Figure 1) that show enhanced coke formation on acid sites at higher Pt content.

The production of significant amounts of benzene requires contributions from both the functions. This is evident from the benzene selectivity data given in Table 2, which shows the benzene selectivity to be negligible for the case of the acid catalyst only. The metallic function provides the necessary dehydrogenation activity, while the acidic function is needed for ring expansion (Zaera, 1986; Weisz, 1962). The selectivity for benzene as a function of time is given in Figure 6 for the different catalysts. The curves show a maximum in selectivity at about 2 h which is followed by a monotonic decline. This behavior can also be explained in terms of the effect of coke

Table 2. Selectivity Data (mol %)*

	Wt. % Pt									
	0.00		0.50		0.75		1.00		1.25	
Reactions	*I*	*F*	*I*	*F*	*I*	*F*	*I*	*F*	*I*	*F*
Hydrogenolysis (C_1)	1	0	6	2	8	2	12	3	19	4
Hydrocracking ($C_2 - C_5$)	64	49	28	20	28	18	22	15	20	11
Ring Opening (iso-and n-C_6)	21	30	18	29	13	26	10	26	8	25
Benzene	2	3	46	41	48	37	51	36	47	34
MCPe+MCPde	0	0	1	5	1	7	2	10	4	14
Cyclohexane	1	3	1	2	1	3	1	3	1	3
Polynuclear Aromatics	0	0	0	1	1	5	2	7	1	9
Olefins	11	15	0	0	0	0	0	0	0	0
<u>Ring Opening Selectivities</u>										
2MP	28	27	39	23	41	22	42	20	46	19
3MP	21	20	25	18	24	17	25	16	24	15
n-C_6	51	52	36	58	35	62	33	63	33	66
$\frac{3\ MP}{n\text{-}C_6}$	0.42	0.39	0.70	0.31	0.69	0.26	0.74	0.25	0.72	0.23

*I = 0.2 h; F = 6 h

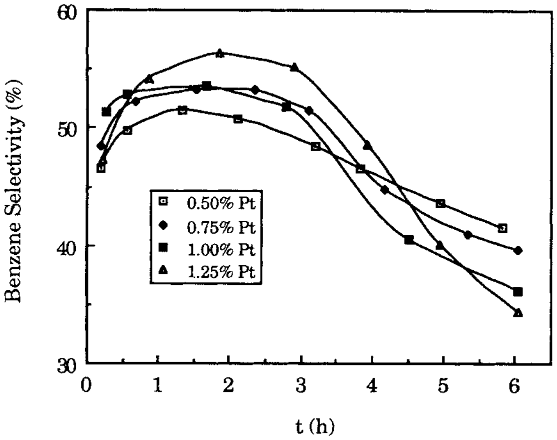


Figure 6. Selectivity for benzene production, requiring participation of both functions, vs. time for different Pt loadings.

deposition on the metal and acid functions involved in the benzene production. As discussed previously, the selectivity for MCPe and MCPde (Figure 1), which are the intermediate products in the benzene pathway, increases initially due to the reduction in C_1 production. This results in an initial increase in the selectivity for benzene with the increase being greater at higher metal loadings. However, after 2 to 3 hours, the increase in MCPe and MCPde selectivity levels off as the amount of coke on the metal function becomes essentially unchanged with a pseudosteady state prevailing due to continuous surface regeneration (Figoli et al., 1983) by catalytic hydrogasification of coke. The support, however, continues to deactivate, thus reducing the number of acidic sites available for ring expansion. This results in decreasing the benzene selectivity at longer times. Since catalysts with higher Pt content experience more extensive coking at the acidic function, the rate of decline in selectivity increases with metal loading.

Figure 7 provides a reaction mechanism for MCP conversion on a bifunctional reforming catalyst, which is a somewhat more detailed version of the scheme given by Parera et al. (1986) and is consistent with the experimental observations described above. As is evident from the results in Table 2, MCP is activated by both the acid and the metal functions. The MCP adsorbed on the metallic function can be transformed by a number of different reaction pathways. These include hydrogenolysis to C_1, dehydrogenation to MCPe and MCPde, and ring opening to hexane and methylpentanes. The MCP adsorbed on the acidic function is transformed by the typical acid catalyzed processes including isomerization, hydrocracking, and hydrogen transfer reactions. Figure 7 also shows the bifunctional catalytic route in the production of benzene.

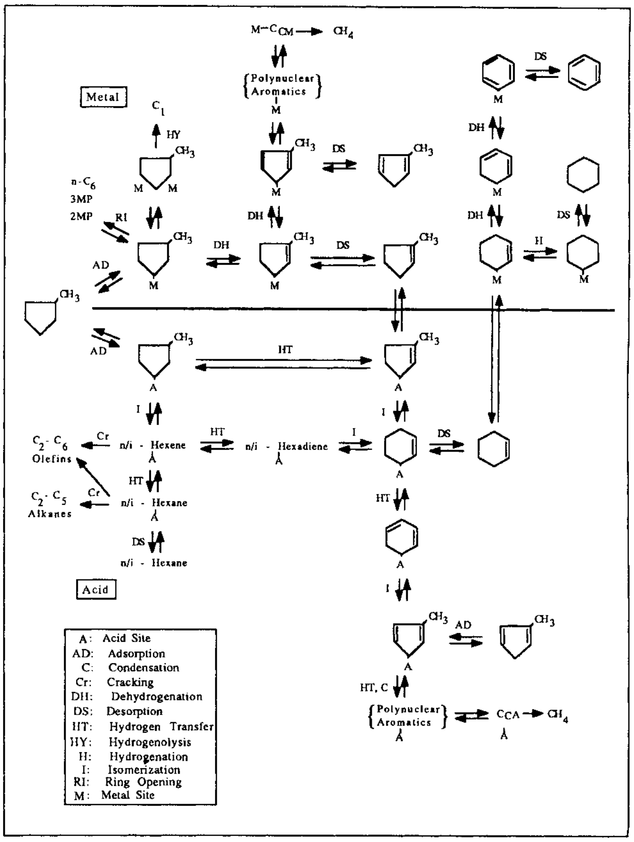


Figure 7. Reaction mechanism for MCP conversion and coke formation on bifunctional reforming catalysts.

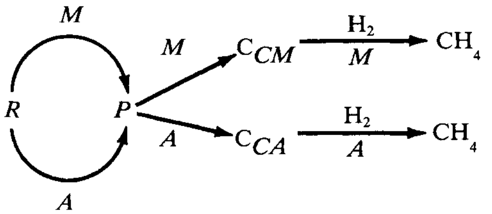
Coke formation on the metal surface occurs through a series of complex reactions. Although coking has been extensively studied (Blackmond et al., 1982; Franck and Martino, 1982; Eberlym and Drushel, 1966), it still is not very well understood. It is generally accepted, however, that coke consists of highly unsaturated polycyclic compounds and that olefins are the precursors to coke (Wojciechowski, 1974). In particular, unsaturated five-carbon-atom-ring compounds such as cyclopentadiene and methylcyclopentadiene (MCPde) are found to be prodigious coke producers (Parera et al., 1984; Barbier, 1986). Figure 7 shows coke formation proceeding through the dehydrogenation of MCP to produce MCPde and its subsequent polymerization to produce coke on the metal and acid sites. Although the details are not shown in Figure 7 for brevity, MCPde can condense by a Diels Alder reaction with another MCPde molecule yielding an indenic structure (Parera et al., 1984), which can then undergo dehydrogenation to form aromatic ring structure. Thus, coking occurs on the metal by the successive condensation of unsaturated five-membered rings followed by metal-catalyzed dehydrogenation to form polyaromatic ring structures. On the acid sites, the hydrogen abstraction proceeds through hydrogen transfer. Regeneration of deactived sites can occur by the hydrogasification of coke molecules to form methane (Parera et al., 1983). This occurs far more readily on the metal sites than on the acid sites. However, hydrogen spillover effect can be important in coke cleaning on the acid sites. It may be mentioned that hydrogasification of coke is relatively slow and is not a major source of methane when compared with the hydrogenolysis reaction.

Theoretical Model

A dual-site model is developed below, which explicitly considers the activity and deactivation of both of the metal and acid functions.

Coking kinetics

Deposition of coke on the catalyst is assumed to proceed according to the following simplified mechanism:



(1)

which is based on Figure 7. The reactant, R, is activated, although to different extents, by the metal and acid sites denoted by M and A, respectively, to produce a common coke precursor, P. This species is then transformed into coke on either the metal, C_{CM}, or on the support, C_{CA}. Site regeneration can occur via coke reduction by H_2 to form methane and can be expected to occur much more readily on the metal rather than on acid. If it is assumed that the concentration of P is proportional to $(M_0 + bA_0)$, where b is a dimensionless constant representing the relative activity of acid sites for precursor formation, the net rate of metal and acid deactivation may be given, respectively, by:

$$r_{dM} = f'_{dM} M_0 s_M (M_0 + bA_0) - k_{HM} M_d C_{\mathrm{H}_2} \tag{2}$$

and

$$r_{dA} = f'_{dA} A_0 s_A (M_0 + bA_0) - k_{HA} A_d C_{\mathrm{H}_2} \tag{3}$$

where the subscript d refers to quantities related to deactivation, f' represents the balance of the rate expression for coke formation, its specifics being immaterial for our purposes here, s is the fraction of vacant sites, k_H is the rate constant for coke removal, and C_{H_2} is the hydrogen concentration. The rate expression for coke cleaning is assumed to be of the form given in Eqs. 2 and 3 for the sake of simplicity. Other forms could be assumed if the site cleaning mechanism were known, which is quite uncertain. Further, in general we may expect k_{HA} to vary with the metal content due to the hydrogen spillover effects. However, it is unlikely that this effect is important under the experimental conditions employed in this study and, therefore, k_{HA} is assumed to be a constant here.

A site balance over the metal phase yields (Lee, 1985):

$$s_M \equiv \frac{M_v}{M_0} = \frac{\alpha_M}{[1 + \sum_i (K_{iM} C_i)^{m_{iM}}]^{n_M}} \tag{4}$$

where the fraction of active metal sites remaining is given by:

$$\alpha_M \equiv \frac{M_0 - M_d}{M_0} \tag{5}$$

Similarly, a site balance over the acid phase yields:

$$s_A \equiv \frac{A_v}{A_0} = \frac{\alpha_A}{[1 + \sum_i (K_{iA} C_i)^{m_{iA}}]^{n_A}} \tag{6}$$

where

$$\alpha_A \equiv \frac{A_0 - A_d}{A_0}. \tag{7}$$

These equations can be substituted into Eqs. 2 and 3 to give:

$$r_{dM} = f_{dM} M_0 \alpha_M (M_0 + bA_0) - k_{HM} C_{\mathrm{H}_2} M_0 (1 - \alpha_M) \tag{8}$$

and

$$r_{dA} = f_{dA} A_0 \alpha_A (M_0 + bA_0) - k_{HA} C_{\mathrm{H}_2} A_0 (1 - \alpha_A) \tag{9}$$

where f'_{dM}, f'_{dA}, and the terms in the denominators of Eqs. 4 and 6 have been incorporated into f_{dM} and f_{dA}, respectively.

Equations 8 and 9 can be used to obtain the time dependence of α_A and α_M, respectively, as follows. The rate of deactivation of the metal can be expressed in terms of α_M by:

$$r_{dM} = -M_0 \frac{d\alpha_M}{dt}. \tag{10}$$

Substituting Eq. 10 into Eq. 8, one obtains:

$$\frac{d\alpha_M}{dt} = \delta_M \left\{ 1 - \alpha_M \left(1 + \frac{1}{\beta_M} \right) \right\} \tag{11}$$

where

$$\delta_M \equiv k_{HM} C_{H_2} \tag{12}$$

and

$$\beta_M \equiv \frac{\delta_M}{f_{dM}(M_0 + bA_0)}, \tag{13}$$

which represents the relative rates of site cleaning and fouling. Using the initial condition that $\alpha_M = 1$ at $t = 0$, Equation 11 can be integrated for constant composition and temperature to give

$$\alpha_M = \frac{1}{1 + \dfrac{1}{\beta_M}} \left[1 + \frac{1}{\beta_M} \exp \left\{ -\delta_M \left(1 + \frac{1}{\beta_M} \right) t \right\} \right]. \tag{14}$$

Similarly, for the acid phase

$$\alpha_A = \frac{1}{1 + \dfrac{1}{\beta_A}} \left[1 + \frac{1}{\beta_A} \exp \left\{ -\delta_A \left(1 + \frac{1}{\beta_A} \right) t \right\} \right] \tag{15}$$

where δ_A and β_A are defined analogous to δ_M and β_M in Eqs. 12 and 13, respectively. Since the reactor conditions actually change with time, the simplifying assumption of constant composition and temperature is a potential source of error. From Eqs. 14 and 15, we see that α is initially unity and decays to a steady-state value of $(1 + 1/\beta)^{-1}$. The rate of decay depends on f_d and δ, whereas the steady-state value of α will depend on their ratio.

The amount of coke deposited on the catalysts can be found by assuming the rate of coke formation to be proportional to the rate of site deactivation. Based on this assumption, for the metal phase,

$$\frac{dC_{CM}}{dt}=W_M\frac{dM_d}{dt}=-W_M M_0\frac{d\alpha_M}{dt} \tag{16}$$

where W_M is a proportionality constant representing the mass of coke deposited per deactivated metal site. Using the initial condition that $C_{CM} = 0$ when $\alpha_M = 1$, Eq. 16 can be integrated to give:

$$C_{CM}=W_M M_0(1-\alpha_M). \tag{17}$$

Similarly, for the acid phase

$$C_{CA}=W_A A_0(1-\alpha_A), \tag{18}$$

where W_A is the mass of coke deposited per deactivated acid site. The total coke on the catalyst is, thus, given by:

$$C_C=W_A A_0(1-\alpha_A)+W_M M_0(1-\alpha_M) \tag{19}$$

Conversion of R

The conversion rate of R is assumed to be first-order in reactant concentration, C_R:

$$-r_R=\phi_{RM}C_R M_0\alpha_M+\phi_{RA}C_R A_0\alpha_A \tag{20}$$

where ϕ is the rest of the rate expression for reactant conversion, and its specific form is not of direct relevance here. It may alternatively be interpreted as the pseudofirst-order rate constant. The first term on the righthand side of Eq. 20 is the rate of conversion of R on the metal, whereas the second term is the rate of conversion on acid occurring in parallel.

For a fixed-bed reactor with plug flow of fluid and a constant molar flow rate of reactant, F_{R0}, a material balance on the reactant R yields

$$\tau=\frac{WC_{R0}}{F_{R0}}=\int_{C_{R0}}^{C_R}\frac{dC_R}{-r_R} \tag{21}$$

where W is the catalyst mass in the reactor and C_{R0} is the feed concentration of R. Substitution of Eq. 20 into Eq. 21 and subsequent integration, assuming α_A and α_M to be uniform along the bed, and rearrangement leads to

$$X=1-\exp\{-\tau(\phi_{RM}M_0\alpha_M+\phi_{RA}A_0\alpha_A)\} \tag{22}$$

where X is the overall conversion of R.

Comparison of model with experiments

The model developed above was used to correlate the experimental data obtained from MCP reforming. The model parameters were estimated by regression of the data in a systematic manner as described below. The number of metal and acid sites for the different catalysts, calculated as described previously, are given in Table 1. The values of the kinetic parameters, δ and f_d, associated with acid and metal activity, α_A and α_M, were determined from C_3 and C_1 data, respectively. As discussed previously, C_3 production is due primarily to hydrocracking reactions on the acid phase, whereas the production of C_1 is due to hydrogenolysis on the metal. The activity for the production of a species, C_i, at a time t is defined as (Butt and Petersen, 1988):

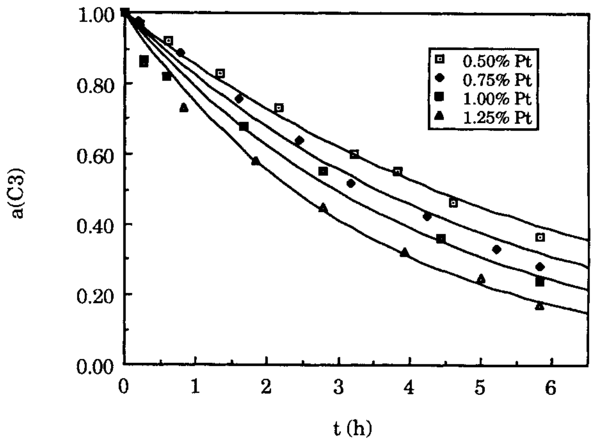


Figure 8. Comparison between experimental and theoretical C_3 activity vs. time for different Pt loadings.

$$a(C_i)=\frac{r_t(C_i)}{r_0(C_i)} \tag{23}$$

where $r_t(C_i)$ is the rate of C_i production at time t and $r_0(C_i)$ is the initial rate on the uncoked catalyst. If a product is formed by a pathway that involves only one catalyst function, then the fraction of active sites for that function can be related to $a(C_i)$ by:

$$a(C_i)=\alpha^n. \tag{24}$$

The value of the exponent n corresponds to the number of sites involved in the rate-determining step (*rds*) in the pathway for the production of C_i.

If a single acid site is assumed to be involved in the *rds* of the reactions leading to C_3 production, then

$$a(C_3)=\alpha_A \tag{25}$$

where α_A is given by Eq. 15. A comparison of Eq. 25 with C_3 production data in the form of $a(C_3)$ vs. time for the different Pt loadings is provided in Fig. 8. The best fit values for the two unknown parameters, δ_A and f_{dA}, were determined by regression of the data. δ_A was thus estimated to be rather small ($\sim 1\times10^{-3}$ h^{-1}) with a relatively large standard error. This means that the rate of coke cleaning by hydrogasification on the acid sites is negligible under the experimental conditions employed here. This, of course, may not be so under industrial conditions when hydrogen spillover may have a considerable effect on the acid site cleaning. At any rate, $\delta_A = 0$ was assumed here for simplicity. For this case, Eq. 15 simplifies to

$$\alpha_A=\exp\{-f_{dA}(M_0+bA_0)t\} \tag{26}$$

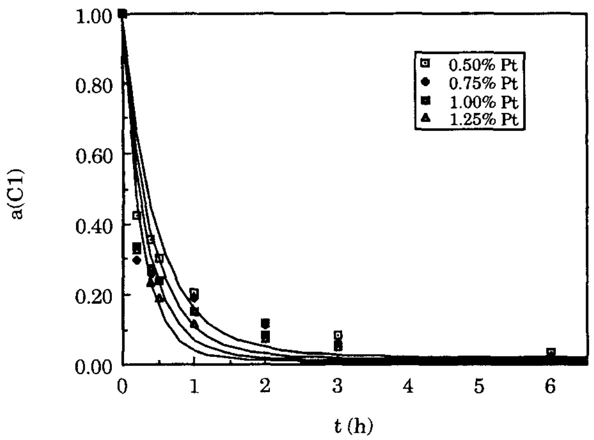


Figure 9. Comparison between experimental and theoretical C_1 activity vs. time for different Pt loadings.

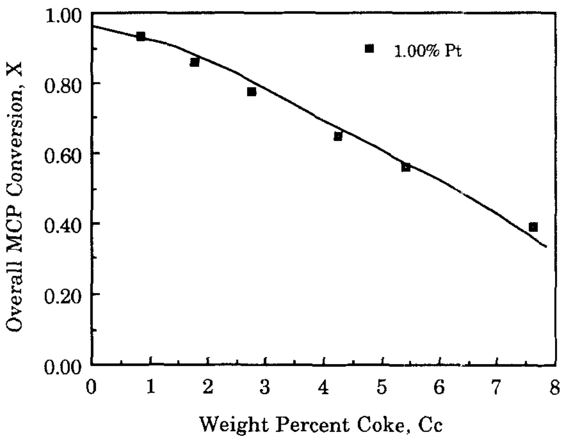


Figure 10. Overall MCP conversion vs. total coke content relationship for 1.00% Pt loading.

The observed relationship is nearly linear.

The other constants were estimated to be $f_{dA} = 8.31 \times 10^{-21}$ g catalyst/(Cl atom·h) and $b = 0.05$. The parameter b was estimated from a regression of the data for the chlorinated support alone, while the calculated values of M_0 and A_0 as given in Table 1 were employed. It is seen that the agreement is quite good ($r = 0.995$) and the model correctly predicts the effect of increasing metal content of catalyst on the reduction in activity for C_3 production.

As discussed before, methane production from MCP hydrogenolysis likely requires more than one metal atom. If we assume that two metal atoms are involved in the *rds*, then α_M and $a(C_1)$ are related by

$$a(C_1) = \alpha_M^2. \tag{27}$$

Bond length considerations indicate that this size requirement is possible, and $n = 2$ provides the most reasonable fit of the data for an *integer* value of n. Figure 9 compares Eq. 27 with C_1 production data in the form of $a(C_1)$ vs. time for the different Pt loadings using the best fit values of the parameters, $\delta_M = 1.66 \times 10^{-1}$ h^{-1}, and $f_{dM} = 5.35 \times 10^{-20}$ g catalyst /(metal atom·h). The model adequately reproduces the general features exhibited by the data although the fit is somewhat less than satisfactory ($r = 0.95$). The fraction of active metal sites, α_M, exhibits a rapid initial drop-off followed by a more gradual decline and essentially reaches a steady state after 2 to 3 hours due to a balance with surface regeneration. The effect of increased metal loading is to cause a larger drop in α_M; however, this effect is more pronounced in the model predictions compared to the data. A better fit may be obtained by using a fractional value between 1 and 2 for the exponent, n, of α_M in Eq. 27.

The relative values of f_{dM} and f_{dA} indicate that metal sites are deactivated more quickly than acid sites: however, coke removal by hydrogasification on the metal function is also much more efficient. Finally, we note that the relative forms of α_M and α_A are consistent with the experimental results of Parera et al. (1988b) under industrial conditions.

Figure 2 compares the model, Eq. 22, with experimental data for the *overall* conversion of MCP as a function of time for catalysts with the different metal loadings. The pseudo-first-order-rate constants for MCP transformation, ϕ_{RM} and ϕ_{RA}, were determined by regression of Eq. 22 to the conversion data and are, $\phi_{RA} = 3.98 \times 10^{-20}$ (Cl atom·h)$^{-1}$, and $\phi_{RM} = 2.67 \times 10^{-19}$ (metal atom · h)$^{-1}$. These results indicate that metal sites are approximately seven times more active than the acid sites in the activation of MCP. As shown in Figure 2, the model accurately predicts the time course of conversion ($r = 0.99$) and the inverse relationship between conversion and Pt content. Initially when the metal surfaces are relatively clean, the model, as may intuitively be expected, predicts that catalysts with higher metal loadings will be more active.

Figure 3 compares the model, Eq. 19, with the experimental data for the total coke deposition on the catalyst as a function of time for the different metal loadings ($r = 0.995$). The values of the parameters W_M and W_A obtained are, $W_A = 5.14 \times 10^{-22}$ g coke /Cl atom, and $W_M = 7.96 \times 10^{-22}$ g coke/metal atom. This indicates that the amount of coke per deactivated site on each phase is comparable and is, in fact, equal to approximately 6 molecules of benzene per metal atom and around 4 molecules of benzene per Cl atom, which appears to be reasonable.

Finally, the overall conversion of MCP is plotted vs. the *total* coke content of the catalyst in Figure 10 for 1.00% metal loading, since such phenomenological relationships are used frequently in the literature. A nearly linear decrease in conversion is observed with coke content. Also shown are model predictions obtained by plotting the conversion computed from Eq. 22 against the coke content from Eq. 19. The fit is representative of that obtained for the other catalysts used. Such observations have prompted investigators to directly relate reactivity to the coke content. Thus, Froment and Bischoff (1979b) have accounted for the influence of coke on the conversion in terms of a deactivation function, $\Phi(C_C)$. This function is an empirical multiplying factor that is used to relate the rate of reaction of R for clean and coked catalysts according to

$$r_R = r_{R0}\, \Phi(C_C) \tag{28}$$

where r_{R0} is the rate when the coke content is zero and r_R is the rate when C_C is the coke content. Several functional forms of $\Phi(C_C)$ have been proposed in the literature, including the linear, $\Phi(C_C) = 1 - \kappa C_C$, the exponential, $\Phi(C_C) = \exp(-\kappa C_C)$, and the hyperbolic, $\Phi(C_C) = (1 + \kappa C_C)^{-1}$ forms. Thus, Figure 10 could be construed as providing support for the linear relationship. It is clear, however, that while such empirical relationships are useful, they provide little insight into the mechanism of deactivation.

Conclusion

The deactivation of bifunctional reforming catalysts and the changes in the selectivity of products formed occur due to the deposition of coke on both the metal and the acid functions. The metallic function deactivates rapidly at first due to coking but then reaches a steady state due to an equilibrium between the rates of coke formation and its removal. Reactions that are demanding, i.e., those requiring sites of more than one contiguous metal atoms, are greatly suppressed, while nondemanding reactions are affected to a lesser extent. The acidic function exhibits a more gradual deactivation behavior with time as coke builds up on the support.

The metallic function largely regulates the amount of coke deposited on itself as well as the amount formed on the support since it is responsible primarily for the production of the coke precursor species (MCPe and MCPde). Catalysts with higher metal loading provide lower overall conversions of the reactant as a consequence of increased precursor formation leading to more coke formation on both the functions. A dual-site model that accounts for the deactivation of both functions is presented here and it adequately describes many features of the experimental behavior. This represents a more fundamental approach to coking and the resulting deactivation of reforming catalysts as compared to the existing models.

Notation

A = acid site
A_0 = total number of Cl atoms initially, Cl atoms/g catalyst
A_d = number of deactivated acid sites, Cl atoms/g catalyst
A_v = number of vacant acid sites, Cl atoms/g catalyst
A_{wA} = atomic weight of Cl
A_{wM} = atomic weight of Pt
$a(C_i)$ = activity for the production of species C_i, Eq. 23
b = ratio of rate of production of P over acid sites and metal sites
C_C = total amount of coke deposited on the catalyst, g coke/g catalyst
C_{CA} = amount of coke deposited on the acid phase, g coke/g catalyst
C_{CM} = amount of coke deposited on the metal phase, g coke/g catalyst
C_i = concentration of species i, mol/m^3; species C_i
C_{R0} = feed concentration of R, mol/m^3
D = metal dispersion, metal atoms exposed/total metal atoms
F_{R0} = molar feed rate of R, mol/h
f_{dA} = rate expression for acid deactivation, g catalyst/Cl atom·h
f_{dM} = rate expression for metal deactivation, g catalyst/metal atom·h
K_{iA} = equilibrium constant for desorption of species i from the acid phase
K_{iM} = equilibrium constant for desorption of species i from the metal phase
k_{HA} = rate constant for acid site regeneration, m^3/mol·h
k_{HM} = rate constant for metal site regeneration, m^3/mol·h
M = metal site
M_0 = total number of exposed metal atoms initially, metal atom/g catalyst
M_d = number of deactivated metal atoms, metal atom/g catalyst
M_v = number of vacant metal atoms, metal atom/g catalyst
m_i = number of molecules of species i adsorbed per site
N = Avogadro's number, 6.02552×10^{23} molecules/mol
n = number of sites in the *rds* of the pathway for C_i production
P = coke precursor (MCPe and MCPde)
R = reactant (MCP)
r = correlation coefficient
r_{dA} = rate of deactivation of acid sites, Cl atom/g catalyst·h
r_{dM} = rate of deactivation of metal sites, metal atom/g catalyst·h
r_R = rate of reaction of R, mol/m^3·g catalyst·h
r_{R0} = rate of disappearance of R initially when the coke content is zero, mol/m^3·g catalyst·h
$r_0(C_i)$ = rate of production of C_i at $t = 0$, mol/m^3·g catalyst·h
$r_t(C_i)$ = rate of production of C_i at time t, mol/m^3·g catalyst·h
s_A = fraction of vacant acid sites, Eq. 6
s_M = fraction of vacant metal sites, Eq. 4
t = time, h
W = mass of catalyst in the reactor, g
W_A = weight of coke deposited on the acid phase per site, g coke/Cl atom
W_M = weight of coke deposited on the metal phase per site, g coke/metal atom
$WHSV$ = weight hourly space velocity, h^{-1}
X = conversion of R

Greek letters

α_A = fraction of active acid sites, Eq. 7
α_M = fraction of active metal sites, Eq. 5
β_A = $\delta_A/f_{dA}(M_0+bA_0)$, ratio of the rates of acid site regeneration and deactivation, Cl atom/metal atom·g catalyst
β_M = ratio of the rates of metal site regeneration and deactivation, Eq. 13, 1/g catalyst
δ_A = $k_{HA}C_{H2}$, related to rate of acid site regeneration, h^{-1}
δ_M = $k_{HM}C_{H2}$, related to rate of metal site regeneration, Eq. 12, h^{-1}
$\Phi(C_C)$ = phenomenological deactivation function, Eq. 28
ϕ_{RA} = rate expression for conversion of R on the acid phase, 1/Cl atom·h
ϕ_{RM} = rate expression for conversion of R on the metal phase, 1/Pt atom·h
κ = constant associated with $\Phi(C_C)$, 1/g coke
τ = weight time, Eq. 21, g catalyst·h/m^3
ω_A = weight fraction of Cl, g Cl/g catalyst
ω_M = weight fraction of Pt, g Pt/g catalyst

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Manuscript received Oct. 31, 1990, and revision received Mar. 25, 1991.