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On the Relationship between Coke Formation Chemistry and Catalyst Deactivation

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A link has been observed between the decline in catalyst activity and coke formation in the cracking of *n*-nonane. The link involves the chemistry and kinetics of the reaction, as well as the chemical structure of coke as observed by ^{13}C CP/MAS-NMR spectroscopy. We find that the chemical structure of surface species normally analyzed as coke plays an important role in the activity of the catalyst. This we believe reflects the influence of the structure of surface carbenium ions on their reactivity in chain propagation and in olefin-forming, site-releasing desorption reactions. Both these processes are vital to the maintenance of catalyst activity. As the average surface species becomes more dehydrogenated, it also becomes less reactive both in bimolecular chain propagation with gas phase reactant molecules and in olefin formation by desorption. This time-dependent loss of reactivity of the average carbenium ion manifests itself in a decline in total catalyst activity with time on stream. © 1992 Academic Press, Inc.

INTRODUCTION

The reaction chemistry and kinetics of the catalytic cracking of *n*-nonane on USHY have been reported previously (*1*, *2*). Mechanistic studies of the system indicate that two mechanisms of cracking are active. One mechanism involves a monomolecular cracking reaction whereby a C–C bond is ruptured by protolysis at an active site on the catalyst. The products formed are a gas phase paraffin and a residual surface-resident carbenium ion. The second mechanism involves a carbenium ion from a previous reaction event abstracting a hydride ion, or a larger fragment, from a gas phase reactant. If this takes place, the erstwhile carbenium ion desorbs as a more saturated (and perhaps larger) species and is replaced on the surface by the carbenium ion of the reactant molecule or some fragment of that ion. This can then crack via β-scission to form an olefin and a smaller carbenium ion, or rearrange and undergo another hydride transfer reaction to form a skeletal isomer. The importance of this bimolecular mechanism to the total conversion activity of the catalyst was found to decrease with increasing temperature.

Kinetic studies of the cracking of *n*-nonane (1) have indicated that surface species composition is very sensitive to reaction temperature. As temperature increases from 400 to 490°C, the reactant carbonium ions compete more effectively for active sites at the expense of adsorbed product species (carbenium ions). This observation is consistent with the conclusion that monomolecular protolysis processes dominate at higher temperatures. The catalyst decay rate was at the same time found to be essentially constant over the temperature range 400°C to 490°C.

Having established an understanding of the chemistry and kinetics of the *n*-nonane system, we can proceed to unravel the mechanism of catalyst deactivation. Most previous studies have centered on relating the decline of catalytic activity to the *amount of* material measured as coke. Our study examines the possibility that it is the

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chemical structure of coke that is the crucial link between coke and the activity of the catalyst.

EXPERIMENTAL

All catalytic reactions were carried out in a plug-flow glass reactor system as described elsewhere (*1, 2*). Samples of coked catalyst were obtained by packing the reactor with 80/100 mesh catalyst mixed with 60/70 mesh silica. At the end of a run the system was purged for 30 min with nitrogen at 100 ml/min. After the purge the reactor was cooled rapidly under flowing nitrogen and transferred to a glove box containing a dry nitrogen atmosphere. There the catalyst was separated from the silica by sieving and packed in an airtight spinner vial. By this means we meant to avoid the effects of oxygen or water on the relaxation process and to avoid any confusion this may cause in interpreting the chemical structure of the coke on the basis of NMR results.

^{13}C CP/MAS NMR spectra were obtained on a Bruker CXP-200 spectrometer. The experimental conditions were:

$$\begin{aligned} &^{13}\text{C CP/MAS} \quad \text{SF} = 50.306\ \text{MHz},\\ &\quad \text{PW} = \pi/2\ (3.5\ \mu\text{sec}),\ \text{ct} = 5\ \text{ms},\\ &\quad\quad \text{RD} = 5\ \text{s},\ \text{SW} = 30\ \text{kHz},\\ &\quad\quad\quad \text{NS} \approx 10{,}000,\ \text{SSR} \approx 3.5\ \text{kHz}. \end{aligned}$$

RESULTS AND DISCUSSION

In considering the relationship between coke and deactivation, we must remember that the coke observed and measured in this study represents those species present on the catalyst at the end of the reaction which did not desorb during the postreaction purge. It thus contains a wide range of species, some of which may have little or no bearing on the loss of catalytic activity, while some poisons may have been stripped from the surface during the postreaction purge. Materials which could have been surface poisons but were desorbed during the postreaction purge may well be among the various alkyl aromatics found as minor products in this and other cracking reactions. A few such species, detected at 400°C in the cracking reactions of *n*-nonane, are presented in Fig. 1. Since it has been shown that the nature and amount of coke depends on the means of measurement (*5–7*), it is difficult to compare the coke properties observed and measured in this study to those observed in other experimental programs. Until an acceptable common definition of coke and a standard method for its determination is found, coke should be viewed as presenting a distorted reflection of the condition of the species present on the surface at the end of a reaction run. In spite of complications, there are many studies of this uncertain material, as it is the only experimentally measurable quantity which may contain information about the chemistry of the deactivation process.

Kinetic modeling of the reaction kinetics and of the decay processes in *n*-nonane cracking on USHY has been presented previously. The decay kinetics were modeled using the general time on stream decay function (*8, 9*). However, mechanistic information about the decay phenomenon cannot be obtained from decay kinetics alone. This is due to the fact that many mechanistic models of decay reduce to the same form of decay expression as that used in this study (*10, 21*). Thus the price of using such a general formulation for the deactivation rate is the loss of ability to discriminate between decay mechanisms. The advantage of the model is that, without prior information about the decay mechanism, the kinetics can be accurately modeled and the rates quantified.

The optimal values of the decay parameters at the three temperatures studied are presented in Table 1. The decay rate constant, represented by the G parameter in the kinetic model, was found to decrease very little over the temperature range examined. The insensitivity of this parameter to reaction temperature confirms the complex nature of the deactivation mechanism in light of the following additional experimental facts:

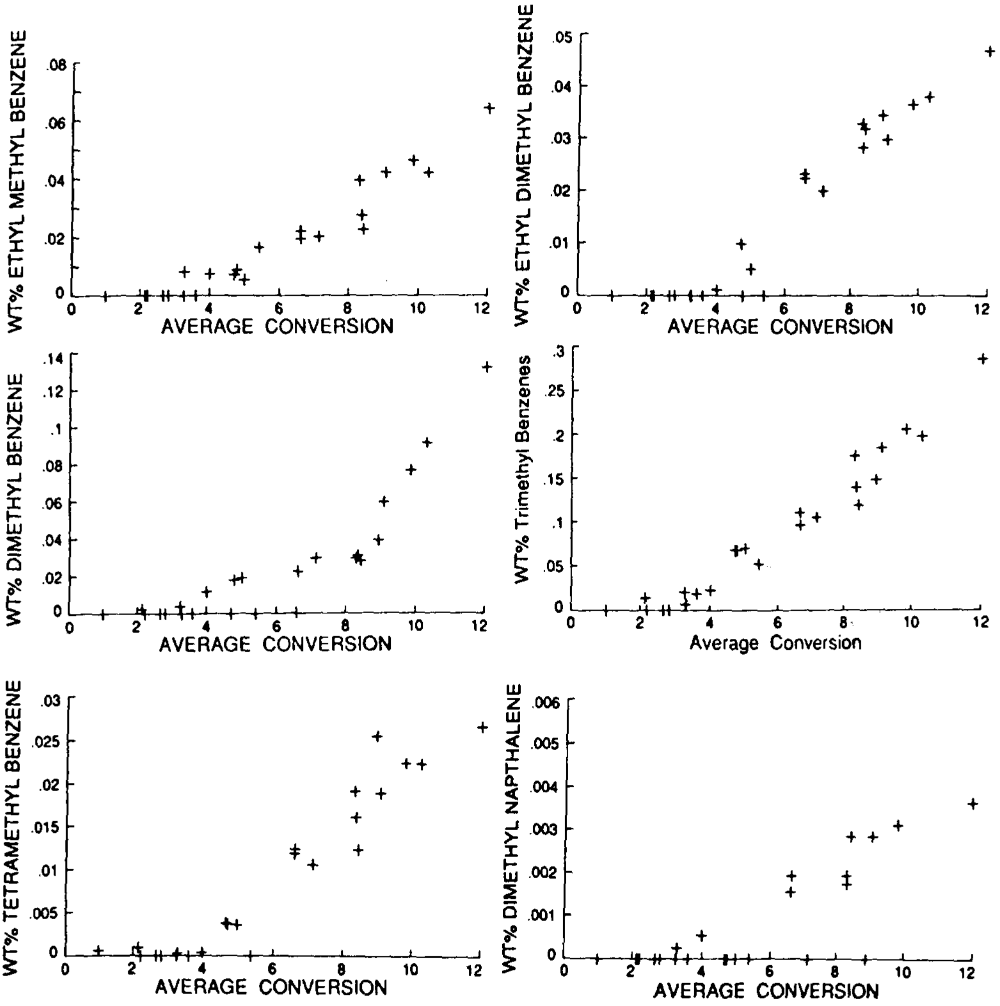

FIG. 1. Selectivity plots of various alkyl aromatic products: (a) dimethylbenzenes; (b) trimethylbenzenes; (c) ethylmethylbenzenes; (d) ethyldimethylbenzenes; (e) tetramethylbenzenes; (e) dimethylnaphthalenes. Each data point represents the individual product yield for the experimental runs at 400°C.

1. there is a somewhat smaller selectivity for coke formation as temperature is increased, as shown in Fig. 2;

2. there are significant changes in the reaction surface composition with temperature, as reflected by the changes in the *B* parameter (*1*);

3. there is a decrease in the contribution of the hydrogen transfer reactions to reactant conversion with increasing temperature, as indicated by both the change in the initial paraffin-to-olefin molar ratio from 1.67 at 400°C to 1.19 at 490°C and the decrease in skeletal isomerization selectivity reported in the mechanistic studies (*2*).

The coke selectivity and kinetic modeling results show that, if a direct relationship between the amount of coke on the catalyst and the activity of the catalyst is to be formulated, then the coke found by measurement must be assigned a more "poisonous" character (per unit weight) as temperature

TABLE 1

Optimal Estimates of Decay Parameters[a] for *n*-nonane

Temperature	G (min^{-1})	N[b]
400°C	5.51 (0.093)	1.0
450°C	5.14 (0.027)	1.0
490°C	4.90 (0.095)	1.0

[a] Approximate standard errors are included in brackets.

[b] The value of the decay exponent, N, was fixed at one in all three cases since the average conversion data exhibit asymptotic behavior as time on stream becomes large.

increases, since the deactivation rate is almost constant over the temperature range studied, while coke yield decreases. It is hard to see how such a parameter can be established without continuously monitoring both the amount of coke and its composition during a reaction. The nature of the coke clearly has an important bearing on its deactivating properties, as well as perhaps influencing the nature of the sites on the framework of the catalyst. One property we have examined is the ^{29}Si MAS-NMR spectrum of the coked USHY, but this showed that interactions between coke and the silicon in the framework are not visible at a statistically significant level (*3, 4*). Another is the nature of the coke itself.

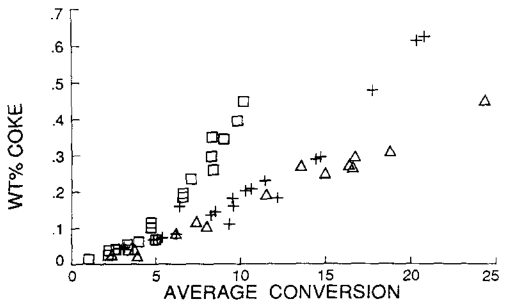

FIG. 2. Selectivity plot for coke formation in the cracking reactions of *n*-nonane on USHY. (□) 400°C; (+) 450°C; (△) 490°C. Each data point represents the yield of coke for an individual experimental run at the temperature indicated.

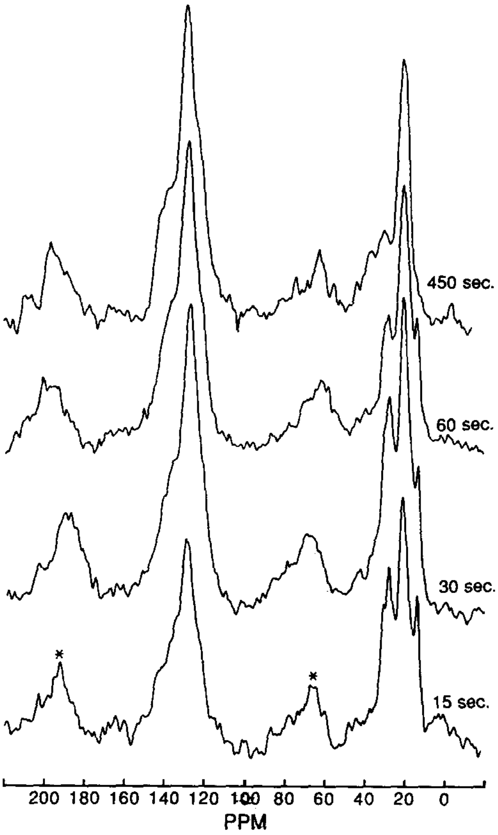

FIG. 3. ^{13}C CP/MAS NMR spectra of coke at 15, 30, 60, and 450 s reaction time, SV = 3.6 g/min/g cat, 400°C. (* denotes spinning side bands at approximately 65 and 195 ppm.)

Figure 3 presents ^{13}C CP/MAS spectra of coke on the catalyst at the end of experimental runs of 15, 30, 60, and 450 s duration at a reaction temperature of 400°C. The structural features observed are similar to those previously reported (*11–14*) using the same technique, although significantly more detail is discernible in the aliphatic region of the spectra presented here. These spectra do not support the often stated view that coke consists solely of polynuclear aromatic species, since there is a substantial signal in the sp^3 region. It can be seen that with increased time on stream the coke dehydrogenates through the rapid loss of primary and tertiary aliphatic carbon groups, as indi-

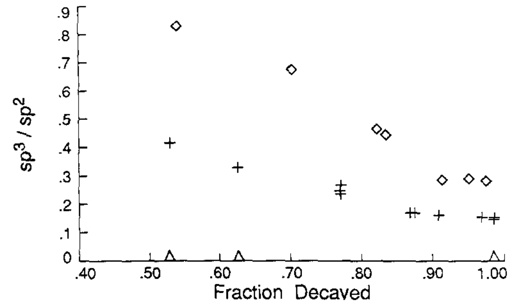

FIG. 4. Ratio of sp^3/sp^2 carbon in coke vs fraction of activity lost by decay as calculated using the TOS decay function and the values of the decay parameters shown in Table 1. (◇) 400°C; (+) 450°C; (△) 490°C.

cated by a decreased signal intensity in the sp^3 region at $\simeq 13$ ppm (methyl groups) and $\simeq 30$ ppm (tertiary carbon groups) relative to the sp^2 region at $\simeq 130$ ppm. A more gradual loss of secondary carbon groups at $\simeq 20$ ppm also occurs. Spinning side bands due to unaveraged chemical shift anisotropy of the sp^2 carbon groups are also present and are identified with an asterisk.

To quantify the observed changes in the spectra, the areas under the sp^2 and sp^3 regions of the spectra were determined. These areas will be proportional to the number of carbon atoms in each configuration, but not directly. Furthermore, their respective constants of proportionality will be different. Figure 4 presents the ratio of the areas under the sp^3 and sp^2 regions of the spectra, plotted as a function of the fractional deactivation of the catalyst predicted by the optimal values of the decay parameters G and N in the expression $1 - 1/(1 + Gt)^N$. The separation process by which the coked catalyst was recovered was not 100% efficient. By using this ratio, we preclude problems associated with obtaining absolute quantities as well as remove the effects of coke loading on the catalyst. For the data at 400°C this ratio is observed to decrease in a linear fashion while catalyst activity decreases from 50% to 10% of its initial value. Unfortunately, the combination of very rapid decay and the limitations of our experimental equipment precluded obtaining reproducible samples of coked catalyst at higher levels of catalyst activity (i.e., shorter time on stream). As the activity of the catalyst decreases below 10% of its initial value, the observed sp^3/sp^2 ratio becomes constant, while with increased temperature the slope of the plot between 50% and 90% decay decreases towards zero. In a previous study with *n*-hexene on USHY at 300°C, Groten *et al.* (*11*) observed that the sp^3/sp^2 ratio in the coke was constant when complete catalyst deactivation is reached. The observation of a constant ratio of sp^3/sp^2 does not necessarily imply that the structure of the coke no longer changes, since the cross polarization experiment does not detect the presence of quaternary carbon atoms. The coke presumably continues to "harden" toward a graphitic form (*15*) with increased time on stream, but does so in the absence of measurable catalytic activity. This process is likely to occur via monomolecular elimination of hydrogen or small paraffins or by some of the radical mediated reactions which have been observed in cracking systems (*16*, *17*). The stability of coke makes it an ideal participant in such less-favored reactions.

We believe the interesting behavior of the sp^3 to sp^2 ratio shown in Fig. 4 is associated with the mechanism of activity decay in the cracking reaction. A surface species has two routes by which it can contribute to conversion and form a gas phase product:

(1) desorption as an unsaturated species;

(2) hydride abstraction from a gas phase molecule accompanied by the release of a more saturated species and replacement of the surface ion by a new carbenium ion.

The ability of a surface species to carry out either of these two reactions will be a strong function of its structure, since it is structure that governs charge distribution (*18*, *19*). The two reactions above are in turn critical to maintaining catalyst activity as they result in either the regeneration of a pristine active site allowing a subsequent conversion event by protolysis, or a chain propagation event which results in a conversion event and leaves behind a species capable of a subsequent chain propagating reaction.

If the structure of a surface carbocation on an active site is changed by a reaction event in a manner such that the new surface species has a greater ability to delocalize its ionic charge, the probability of a desorption event or a chain propagating reaction occurring at that site will decrease. Given the likelihood of random occurrences of this type of reaction, it is reasonable to expect that a relationship will exist between the chemical structure of the average surface species which populate the surface and the activity of the catalyst. Such structure–reactivity relationships are in fact fundamental to many mechanistic postulates made in physical organic chemistry *(18, 20)*. These relationships will no doubt also play a role in the propagation and desorption reactions in this system. As the ratio of sp^3 to sp^2 bonded carbon atoms in the coke decreases, the surface species on average have a greater ability to delocalize their ionic charge and thus become less reactive to both chain propagation and desorption reactions. Our experimental evidence shows that this process proceeds as a function of catalyst time on stream. This is not surprising, since the surface of the catalyst finds itself in a bath of near-constant composition from which various species settle on active sites.

The population of carbenium ions on the surface constitutes the reactant from which catalytic coke is made. The conversion of these surface species to coke proceeds as if they were in a batch reactor where the time of reaction is the time on stream. The overall effect is to make coke and to dehydrogenate it, which leads to a decrease in the instantaneous activity of the average surface site, be it by a decrease in the rate of chain propagation by the formation of less active unsaturated carbenium ions, or by the formation of completely inactive species which remove the site from all participation in conversion reactions and results in catalyst decay. This structure–reactivity relationship provides a link between the activity of the catalyst as predicted by the decay function and the nature of the coke formed on the catalyst.

With increased reaction temperature, the observable changes in the structure of the coke becomes less evident, and at 490°C the ratio of sp^3 to sp^2 carbon is approximately constant with catalyst activity over the range examined. The transition to a constant sp^3/sp^2 ratio occurs more rapidly as temperature is increased and is apparently complete before the catalyst is 50% deactivated at 490°C. With increased temperature, the reaction mechanism also shifts to one where monomolecular cracking events dominate. Changes in the value of the B parameter from kinetic modeling *(1)* indicate that at 490°C the reactant competes equally with products for adsorption sites. Selectivity data for the same system show a lower selectivity for isomeric products, as well as a decreased paraffin-to-olefin ratio, consistent with a decreased importance of chain reactions. Thus the chain cracking process becomes less important to overall conversion as reaction temperature increases. For a species to prevent a catalyst site from carrying out protolytic cracking, it need only cover the site. Thus, structural features which lead to a very low probability of desorption will be important to the high temperature deactivation mechanism. The NMR spectra indicate that it is species with sp^2 carbon which can neither desorb nor undergo a hydride transfer reaction at 490°C. We propose that it is the sp^2 component of the surface species which is important to deactivation under these conditions.

As defined in this study, coke represents material which has essentially zero probability of undergoing a desorption event at reaction temperature, since the postreaction purge fails to induce such an event. The ability to desorb will be a function of the stability of the surface species at the temperature in question. At higher temperatures only a highly dehydrogenated species can delocalize the charge to the extent necessary to have zero probability of desorption. At lower reaction temperatures, the extent of dehydrogenation required to reach this point is smaller. The flat portion of the plots at 400°C and 450°C in Fig. 4 show that the probability of desorption becomes zero at a higher hydrogenation state at lower temperatures. The hydride transfer rate is not zero at this condition; it is at steady state as the coke continues to evolve and the cracking reaction continues. Catalytic cracking may well be proceeding on some of the species observed as coke. Reactions with the unsaturated ions will involve the formation of a large variety of secondary dehydrogenated products, including a range of aromatic species (*11*) as shown in Fig. 1.

In the light of these considerations, the validity of the decay function $(1 + Gt)^{-N}$ used in the kinetic expression should be examined. Recently Rice and Wojciechowski (*21*) reported on the theory and simulations of systems undergoing deactivation via the decreasing reactivity of surface species in the manner described above. They also considered the possibility that sites on their way to complete deactivation can undergo reactivation by the desorption of the inhibiting species, as would be the case if a dehydrogenated surface species manages to abstract a hydride from a gas phase molecule and desorb. They found that, whether site activity is lost by sudden death, as in the original formulation of the time on stream decay function (*8*, *9*), or by decreasing reactivity, as suggested by the above examination of the *n*-nonane system, the time course of catalyst decay can be described by the hyperbolic decay function first proposed in the time-on-stream formulation. The decay kinetics apparently reduce to the general time-on-stream decay function regardless of what portion of the total decay rate is due to sudden death and what portion to the type of gradual inhibition discussed above.

CONCLUSIONS

Correlation of the sp^3/sp^2 ratio for coke, based on ^{13}C CP/MAS NMR spectroscopy, with the predicted catalyst activity, based on the Time-on-Stream decay model, suggests that a relationship exists between the two. An approximately linear decrease in the sp^3/sp^2 ratio with decreasing catalyst activity was observed at 400 and 450°C between 50 and 90% decay. As complete deactivation is approached, this ratio becomes constant. We conclude that the structure of coke, and in particular its degree of dehydrogenation, plays an important role in the deactivation of cracking catalysts. We suggest that this is due to a structure–reactivity relationship which governs the activity of surface species towards both chain propagation and desorption, and consequently governs catalyst activity. As the average surface species becomes more dehydrogenated with time on stream, its reactivity towards desorption or disproportionation decreases. The net effect of this process is an observed decline in the activity of the catalyst which is governed by the length of time the catalyst is in the presence of reactants.

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