Formation of Coke and Minor Products in 2-Methylpentane Cracking Over USHY

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The formation of coke and minor products in 2-methylpentane cracking on USHY has been examined at 673, 723, and 773 K. The results show that the coke precursors are various dehydrogenated carbocations on catalyst surface. Despite the increase of coke yield with reaction time, the selectivity and H/C atomic ratio of coke decrease with rising temperature. Echoing to the formation of coke, minor products including acyclic paraffins, acyclic olefins, methylcyclopentane, diolefins, cyclic olefins, and aromatics are formed by various side-reactions of carbenium ions, such as dehydrogenation, elimination, disproportionation, cyclization, and aromatization. Undergoing of such pathological reaction processes gradually lead to catalyst deactivation. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 750–755, 2008

Keywords: 2-methylpentane, catalytic cracking, coke, minor products, catalyst deactivation

Introduction

Catalytic cracking is one of key processes in upgrading of heavy hydrocarbon fractions to fuel oil.[1–3] The catalytic cracking of hydrocarbons normally proceeds on solid acid catalysts such as zeolites.[4–6] It is well recognized that active intermediates in the catalytic cracking includes various electron-deficient carbocations, which could be classified into two distinct classes: classical trivalent carbenium ions and nonclassical pentacoordinated carbonium ions.[7–10] These carbocations can engage in various "fruitful" mainline processes for feed conversion, but can also be distorted by various "pathological" sideline processes for coke formation.[11]

Most cracking catalysts suffer from deactivation, i.e. the loss of activity and/or a change of selectivity, with time on stream (TOS). The deactivation of catalyst can occur by various chemical and physical mechanisms, which cause the loss of active sites, of surface area, and/or an increase in mass transfer resistance. The catalysts decay due to coke formation is of prime interest both in refinery industry and in scientific research.[12–17] The large loss of catalyst activity could have a disastrous influence on the engineering and commercialization of catalytic cracking technology.

"Coke" is a common generic name given to nonvolatile carbonaceous materials that are formed on the catalysts and in the reactor during reactions. In fact, the definition of "coke" is arbitrary and vague, even though the consequences of coking on catalysts are well recognized. It is known that the composition of coke is affected by a range of variables including reactant and product natures, catalyst acidities, reaction temperature and time, etc. Coke therefore has a broad range of properties dictated by this range of variables. The literature agrees that coke mainly consists of polyaromatic moieties.[18] In the work of Froment et al. on catalytic cracking of vacuum gas oil,[19] coke was considered to consist of five or more aromatic rings and of a total number of C atoms exceeding 40.

The macro-kinetics of catalyst decay in catalytic cracking has been amply demonstrated to be a function of the time of catalyst exposed to reactants, i.e. TOS.[13,20] However, the micro-mechanism of the decay process is still an issue under investigation. Froment[19] and Marin[21] suggested three-ring aromatic molecules as the coke precursors and developed a single-event micro-kinetic model to account the coke formation. Evidently, more work remains to be done for a fundamental

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understanding of the mechanism of coke formation, which involves various elementary reactions.

The deactivation phenomenon in catalytic cracking is not an isolated event but rather the result of various side-reactions, which coexist with the main-reactions. Both mainline and sideline reactions proceed via carbocations on active sites of catalyst, but follow different reaction pathways.[11] The mainline reactions contribute to the conversion of feed hydrocarbons, while the sideline reactions cause the formation of coke and of various minor products. Therefore a better appreciation of carbocation chemistry in catalytic cracking is the key to understand the process of deactivation. A thorough analysis of coke and minor products should provide us with an insight into the mechanism of catalyst decay, just as a complete analysis of the major products has lead us a fuller understanding of the mainline processes.

In this study, we will examine the formation of coke and minor products in 2-methylpentane cracking on ultra-stable HY zeolite (USHY) at 673, 723, and 773 K. By a thorough analysis of minor product and coke composition, our focus is to reveal the chemistry whereby the carbenium ions stray from main-reaction pathways into side-reaction blind alley to be distorted, causing the formation of coke and catalyst decay.

Experimental

Materials

The feedstock, 2-methylpentane of 99% purity was obtained from Aldrich and used as received. The main impurity was 3-methylpentane (0.55%).

HY zeolite was prepared from NaY (BDH Chem.) according to the procedures described in the literature.[22] The HY zeolite was then stabilized by steaming at 673 K for 24 h to produce USHY. Since the dealumination could occur during the steam treatment, the extra-framework aluminum (EFAl) in the steamed HY was removed by extracting EFAl using $(NH_4)_2SiF_6$ (AHF). Ten grams of USHY was placed in a flask containing 0.75 cm^3 of 0.8 M ammonium acetate, and 27 cm^3 of 0.5 M AHF was added slowly with stirring, giving a final pH of 6.5. The mixture was stirred for 3 h at 353 K. The catalyst was then filtered and washed thoroughly (15 washes, with final one lasting 12 h) at 313 K with distilled water. After it was dried overnight in an oven at 383 K, the EFAl-free USHY sample was pelletized, crushed, and sized to 60–80 mesh to be used in all experiments.

The final EFAl-free USHY sample showed good crystallinity with the unit cell parameter of 24.455 Å (10^{-10} m), determined by X-ray diffraction. X-ray diffraction measurements were proformed on a STOE STADI Z/PL instrument using CuKa monochromatic radiation. As_4O_6 was used as an internal standard. The framework Al number of the sample is 26 per unit cell and the framework Si/Al ratio is 6.35, estimated according to Kerr and Dempsey's equation in the reference.[23] Also, the sample has a surface area of 485 m^2/g.

Reaction experiment

All experiments were performed in a fixed-bed plug-flow glass reactor. The catalyst bed (0.15 m long) contains the catalyst diluted with silica in order to minimize any thermal effects of the reaction heat. The reaction runs were done by pumping a set quantity of feed over the catalyst charge at a certain temperature. After each run, the reactor was purged with dry N_2 for 20 min. All unpurged residues were regarded as coke. To regenerate the catalyst with measuring the amount of coke during a run, carbon dioxide-free air was passed through the catalyst at 773 K. The water formed was collected in two drierite tubes in series and the carbon dioxide in two ascarite tubes. Complete combustion to carbon dioxide was assured by passing the dried combustion stream through a reactor containing a combustion catalyst. The hydrogen and carbon contents of the coke were calculated from the collected weight of water and carbon dioxide. Before the experimental runs were carried out, more than 20 replicate runs at 773 K with a TOS of 725 s and Cat/Oil ratio of 0.009 were carried out to examine the activity of the USHY catalyst after regeneration. The results showed good reproducibility of the feed conversion, confirming that the catalyst has good stability under these conditions, and that the regeneration of catalyst is reproducible.[24]

Each catalyst charge was exposed to five or six such runs, each run at a different pumping rate but with the total feed introduced kept constant. This produced runs with constant catalyst/oil ratio and various run durations (or times on stream). The whole procedure was repeated on a series of catalyst charges differing in the amount of catalyst placed in the reactor and then repeated at various temperatures.

Product analysis

Products were identified by a GC/MS. The gaseous products were analyzed using a Carle SX chromatograph which enables the direct determination of hydrogen. The liquid products were analyzed using a Varian capillary chromatograph with a flame ionization detector.

Theory

Chain mechanism

Catalytic cracking of 2-methylpentane on USHY was found to proceed via a chain mechanism,[25,26] consisting of three main steps: chain initiation by protolysis of C—C and C—H bonds in feed molecules on Brønsted acid sites of the catalyst, chain propagation by disproportionations between feed molecules and carbenium ions resident on the surface of catalyst, and chain termination by desorption of carbenium ions as olefins, leaving a proton to reconstitute the Brønsted site for further initiations.

Other reactions accompanying the main chain processes include the rearrangement of carbenium ions leading to isomer production, β-cracking of carbenium ions leading to "excess" olefin production, and interaction between adjacent carbenium ions leading to the formation of coke and minor products as well as the deactivation of active sites.

The kinetic model describing this chain mechanism has been successfully applied to quantitative interpretation of several paraffins cracking on HY zeolite,[25–29] even though the detailed mechanism of coke formation still needs to be fully elaborated in terms of a fundamental understanding of the carbenium ion reactions involved.

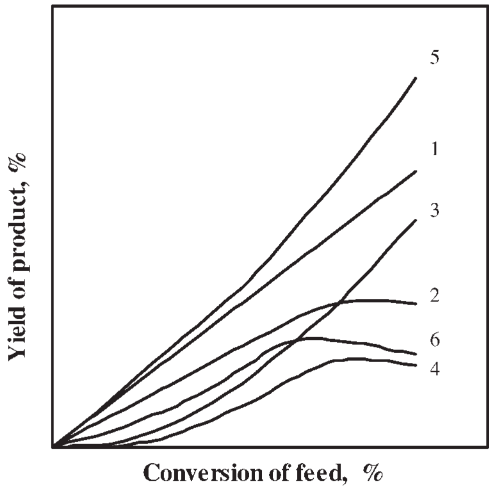

Figure 1. OPEs and selectivity patterns: (1) stable primary product; (2) unstable primary product; (3) stable secondary product; (4) unstable secondary product; (5) stable primary plus secondary product; (6) unstable primary plus secondary product.

Table 1. Initial Weight Selectivities of Primary Products from 2-Methylpentane Cracking Over USHY at 673, 723, and 773 K

	Temperature (K)		
Product	673	723	773
Hydrogen	0.0003	0.0008	0.0023
Methane	0.0027	0.0028	0.0031
Ethane	0.0017	0.0016	0.0030
Ethylene	0.0059	0.0068	0.0124
Propane	0.0923	0.1510	0.2170
Propylene	0.0975	0.1694	0.2900
Isobutane	0.0562	0.0609	0.0820
n-Butane	0.0199	0.0214	0.0217
Isobutene	0.0040	0.0090	0.0220
trans-2-butane	0.0038	0.0041	0.0094
cis-2-butane	0.0020	0.0030	0.0080
Isopentane	0.0800	0.0870	0.0950
n-Pentane	0.0063	0.0055	0.0033
C_5-Olefins	0.0065	0.0080	0.0032
2,3-Dimethylbutane	0.0899	0.0690	0.0382
3-Methylpentane	0.4338	0.3044	0.1210
n-Hexane	0.0491	0.0460	0.0210
C_6-Olefins	0.0401	0.0420	0.0410
Coke	0.0080	0.0074	0.0065
Total	1.0000	1.0000	1.0000

Selectivity patterns

Selectivity data could be useful in evaluating the quantitative aspects of the cracking reaction mechanism. An effective methodology for determining the initial selectivities of products from experimental yield and conversion data was well established by Wojciechowski et al.[13,26] This method involves plotting the time-averaged yield of each product against the time-averaged conversion of feed. Each of the plots is then enveloped by a single curve, called the optimum performance envelope (OPE) which describes the selectivity behavior of that product as catalyst decay approaches zero. According to the initial slope and subsequent curvature of the OPEs, all the products can be selectively classified as six categories, as shown in Figure 1. For examples, a product is considered primary if the slope at the origin of its OPE is nonzero and secondary if the slope is zero. Primary products are those products formed from the feed molecule without any detectable gas-phase intermediates. OPEs which exhibit a maximum with conversion belong to unstable products; those which increase linearly with conversion belong to stable products; and those which curve up belong to products which arise in both primary and secondary reactions.

Results and Discussion

Formation of primary products

Table 1 gives the initial selectivities of all primary products in 2-methylpentane cracking on USHY at 673, 723, and 773 K. The primary products from the conversion of 2-methylpentane at 673 K include paraffins in the range C_1-C_5, olefins in the range C_2-C_6, three C_6 isomeric paraffins (3-methylpentane, 2,3-dimethylbutane, and *n*-hexane), H_2, and coke. The selectivity distribution of primary products varied with the reaction temperature. For examples, the selectivity of C_6 isomeric paraffins decreased from 57.3% to 18.0% and that of propane plus propylene increased from 19.0% to 50.75% with increasing temperature from 673 to 773 K. In a series of previous studies,[25,26,28] we have presented a quantitative interpretation to the selectivity patterns and variation of the primary products from 2-methylpentane cracking on USHY, based on the chain mechanism of carbocations reactions. However, we did not examine the details of the coke forming process due to the complexity of this subject.

Formation of coke

There continues to be our interest to study the mechanism of coke formation and catalyst decay in hydrocarbon catalytic cracking. Figure 2 show the OPE curves of coke in 2-methylpentane cracking on USHY at 673, 723, and 773 K. One can see that the coke is formed as a primary plus

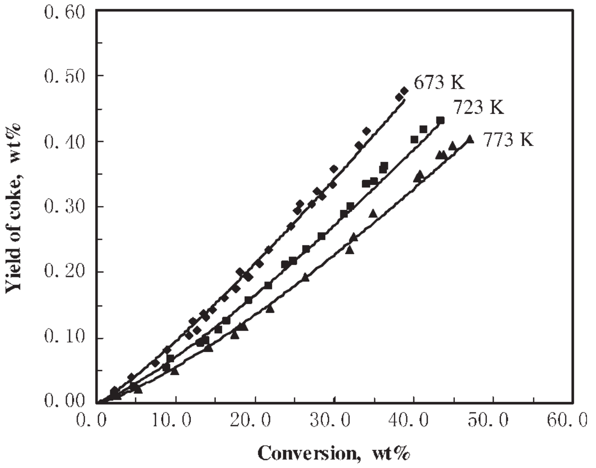

Figure 2. Optimum performance envelops of product coke from 2-methylpenatne cracking on USHY at 673, 723, and 773 K.

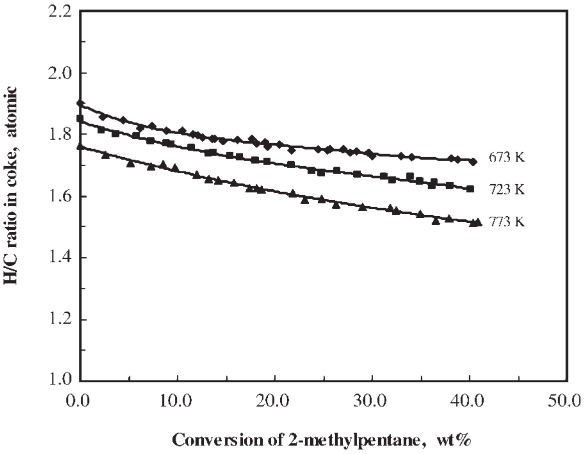

Figure 3. H/C atomic ratio of coke varying with conversion of 2-methylpentane cracking on USHY at 673, 723, and 773 K.

secondary product (pattern 5 in Figure 1), the yield of coke was increased with the feed conversion at all three temperatures, but the weight selectivity of coke formation (the slope of OPE curve) was decreased with rising temperature. The decrease of coke selectivity with increasing temperature seems a little surprising, but becomes quite understandable if we recognize that coke is the product of inter-reaction between carbenium ions on surface of the catalyst. Since there are fewer such species on the catalyst surface due to the increase of their desorption rate at high temperature, the rate of coke formation will decrease with rising temperature.

It must be clarified that the definition of "coke" is arbitrary, and the structure of coke is not fully defined. The coke formed in catalytic cracking of hydrocarbon is not a pure compound but rather a mixture (or pseudocomponents) of various nonvolatile hydrocarbons, and the precursors are various unsaturated carbenium ions. Therefore, the formation of coke undergoes a series of reaction processes, and the composition of coke varies with reaction conditions. As shown in Figure 3, the H/C atomic ratio of coke produced in 2-methylpentane cracking on USHY decreases with increasing the conversion and reaction temperature. The H/C ratio in initial coke is 1.93 (close to the H/C ratio of 2 in olefins) at 673 K, 1.84 at 723 K, and 1.76 at 773 K. As the conversion of feed 2-methylpenatne increased to 40% corresponding to increase reaction time, the H/C ratio was decreased to 1.71, 1.62, and 1.52 at 673, 723, and 773 K, respectively.

The above results indicate that the "pre-coke" consists largely of carbenium ions on catalyst surface at initial stage of reaction and lower temperature. With increasing reaction time or temperature, these ions become more unsaturated by various pathological processes, such as dehydrogenation, cyclization, and aromatization. These processes compete the surface ions with the fruitful processes for feed conversion. As a result, the processes of coke formation cause a gradual loss in the activity of reaction sites.

Formation of minor products

Various minor compounds were formed as secondary products in cracking of 2-methylpentane over USHY. The formation of these minor products is closely related to the formation of dehydrogenated ions, i.e. coke precursors. They in fact constitute byproducts of coke formation reaction. Therefore, an analysis of minor products is essential to a fundamental understanding of the mechanism of catalyst decay due to coke formation.

As presented in Table 2, minor products from the catalytic cracking of 2-methylpentane over USHY at 25% feed conversion consist of acyclic paraffins, acyclic olefins, methylcyclopentane, diolefins (trace), cyclic olefins (trace), and aromatics. Acyclic paraffins include 2,2-dimethylbutane and C_7 paraffins (2-methylhexane, 3-methylhexane, and heptane), and acyclic olefins include normal, methyl, and dimethyl C_7 and C_8 olefins. Aromatic products consist of various alkylated benzenes with carbon numbers from 7 to 9, and alkylated naphthalenes with carbon numbers from 11 to 13. The yields of minor products were found to decrease with increasing temperature, echoing to the variation of coke yield with reaction temperature.

It is interesting to see that only trace amount of diolefins and cyclic olefins (yield $< 0.0005\%$) were found in products of 2-methylpentane cracking over USHY at 25% conversion. This indicates that diolefinic ions and cyclic olefin ions are hard to desorb from the catalyst surface and easily undergo subsequent dehydrogenation reactions to become more unsaturated aromatics and further to form coke.

Catalyst decay as a side reaction of carbenium ions

On the basis of the analysis of minor products and the decreases of H/C ration in coke with reaction time and temperature, we propose that the catalyst decay in 2-methylpentane cracking on USHY was accompanied with the reactions of surface ions which could yield products in the following sequence:

Alkanes → Alkenes → Diolefins → Cyclic olefins → Aromatics → Polyaromatics

The above reaction sequence suggests that the surface ions become more and more unsaturated, causing the reactivity loss of the sites step by step. In previous studies,[25,26] we

Table 2. Yield (wt %) of Minor Products from Reaction of 2-Methylpentane Cracking Over USHY at 25 % Conversion

	Temperature (K)		
Product	673	723	773
2,2-Dimethylbutane	0.1140	0.1050	0.0414
Methylcyclopentane	0.0430	0.0240	0.0060
C_7-Paraffins[a]	0.3930	0.2050	0.1580
C_7-Olefins	0.1580	0.1070	0.0820
Toluene	0.0450	0.0420	0.0370
C_8-Olefins	0.0880	0.0400	0.0123
Diolefins	tra[b]	tra[b]	tra[b]
Dimethylbenzene	0.2180	0.1880	0.1080
Trimethylbenzene	0.0933	0.0750	0.0450
Ethyldimethylbenzene	0.0230	0.0170	0.0080
Methylnaphthalenes	0.0020	0.0030	0.0030
Dimethylnaphthanenes	0.0030	0.0040	0.0040
Trimethylnaphthalenes	0.0030	0.0040	0.0020
Total	1.1833	0.8140	0.5067

[a] Including 2-methylhexane, 3-methylhexane, and heptane.
[b] Trace amount (<0.0005).

have discussed how the varieties of saturated carbenium ions participate in the fruitful reactions of chain mechanism such as isomerization, and disproportionation with feed molecules. The same carbenium ions, however, also involve some pathological reaction processes such as decompositions, and disproportionation with neighbors ions. These undesirable processes produce unsaturated carbeniums which, we believe, are responsible for coke formation and hence catalyst decay. These side reactions also result in the formation of minor products. It is widely understood that the minor products, including coke, consist of complex molecules. Consequently, their formation must be severely hindered by the steric requirements of their transition states. This fact alone is probably enough to explain the rarity of these processes.

The following discussion on several pathological reactions on catalyst surface will give us a clue to the mechanism of catalyst decay in hydrocarbon cracking.

Decomposition or elimination

A larger carbenium ion enables to form a smaller hydrocarbon molecule by a direct monomolecular elimination (decomposition) reaction, leaving behind a carbenium ion containing a double bond, i.e. an olefin-ion that is

$$\mathrm{C}_n\mathrm{H}_{2n+1}^{+}\mathrm{S}^{-} \;\rightarrow\; \mathrm{C}_{n-j}\mathrm{H}_{2(n-j)-1}^{+}\mathrm{S}^{-} + \mathrm{C}_j\mathrm{H}_{2j+2} \tag{1}$$

where *S* represents an active site on catalyst surface.

The double bond of an olefin-ion can then undergo a protonation at a neighboring site to form a bridging di-ion. Alternatively it can cyclize on the original site to form a cyclic carbenium ion. If the olefin ion does not desorb and remains attached at the site where it forms without undergoing further chain-propagating reactions, it will be responsible for coke formation. Such an event will prevent one site from participating in the conversion processes responsible for the fruitful reactions, and therefore will contribute to a first-order deactivation of overall activity.

Ion–ion disproportionation

Ion–ion disproportionation may take place between two adjacent carbenium ions on the surface if the charge centre of one ion interacts with the neutral end of the other ion. In such a disproportionation, a negative moiety leaves one reactant ion and attaches itself to the other. The ion receiving the moiety becomes neutral and desorbs as paraffin, while the other ion will be left behind as a di-ion with the positive charges of the original ion and of the departing ion. The di-ion formed in this way is attached at two sites and arises by a process which is clearly a minor reaction, that is

$$\mathrm{C}_n\mathrm{H}_{2n+1}^{+}\mathrm{S}^{-} + \mathrm{C}_m\mathrm{H}_{2M+1}^{+}\mathrm{S}^{-} \longrightarrow {}^{-}\mathrm{S}^{+}(\mathrm{C}_n\mathrm{H}_{2n})^{+}\mathrm{S}^{-} + \mathrm{C}_m\mathrm{H}_{2m+2} \tag{2}$$

The doubly charged species may well be very resistant to desorption, making the two sites of attachment unavailable for further reaction. Such a mode of decay will be evidenced by a second-order reaction of deactivation.

Occasionally such a bridging di-ion can release its attachment at one site by giving up a proton to reconstitute one of the Brønsted acid sites, thereby creating an olefin-ion on the other site, as shown in Eq. 3. The olefin-ion resulting from this event can lead to the formation of cyclic products, or desorb as a diolefin, as illustrated in Eq. 4.

$${}^{-}\mathrm{S}^{+}(\mathrm{C}_n\mathrm{H}_{2n})^{+}\mathrm{S}^{-} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n-1}^{+}\mathrm{S}^{-} + \mathrm{H}^{+}\mathrm{S}^{-} \tag{3}$$

$$\mathrm{C}_n\mathrm{H}_{2n-1}^{+}\mathrm{S}^{-} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n-2} + \mathrm{H}^{+}\mathrm{S}^{-} \tag{4}$$

Cyclization

An olefin-ion will be able to cyclize in a "head to tail" reaction to form a cyclic, saturated carbenium ion if the steric constraints of the catalyst pores will allow the necessary rearrangement. This process will take place only if the segment between the double bond and the carbon on which the charged resides is long enough, so that the pore dimensions must be large enough to permit a fairly bulky configuration to be achieved.

Such cyclic saturated ion can desorb as a cyclic monoolefin, or, after further H_2 or paraffin eliminations, as a cyclic diolefin or aromatic. This is the reaction which constitutes the initial step in the formation of aromatics in large pore zeolites. Since few cyclic diolefins are found in the product, we can assume that once a cyclic olefin ion is formed, subsequent eliminations leading to an aromatics ion are very easy.

Aromatization and polycondensation

Once a long-lasting surface species such as an ion-bridge is formed by a doubly-charged ion, either end of this di-ion may undergo a subsequent disproportionation with a neighboring carbenium ion, add a product olefin, or disproportionation with a gas phase paraffin. The olefin addition and surface disproportionation with a neighboring ion would seem to be the most common reactions. Such events will enlarge the ion-bridge or extend it to encompass three charged sites. The process can continue, with the surface species becoming larger, attached to more sites, and less desorbable.

Given enough time, the ion-bridge network will become an island of dehydrogenated poly-ionic species, very hard to desorbs and increasingly inactive for further disproportionation due to increasing resonance in the structure. Internal rearrangement to minimize the potential energy of this ensemble will encourage the elimination of small saturated moieties, mostly hydrogen and methane. The resultant "island" will therefore become more unsaturated and begin to resemble complex condensed aromatics. Since all these processes are slow, it is not surprising that highly condensed aromatics in coke are generally found at long times on stream.

Summary and Conclusions

An investigation of the formation of coke and minor products in 2-methylpentane catalytic cracking at 400–500°C has revealed a number of important features concerning the side-reactions of carbenium ions on the active sites of USHY cracking catalyst. Examination of the chemistry of various pathological reactions involving carbenium ions lead us a better understanding of the mechanism of catalyst deactivation.

We find that the coke is formed as a stable primary plus secondary product, and its yield is increased with the feed conversion, but its selectivity is decreased with rising reaction temperature. On the other hand, the H/C atomic ratio in coke decreases with increasing either the feed conversion or reaction temperature. The results indicate that as reaction temperature increased the coke precursors on catalyst surface become more unsaturated by various pathological reactions, but their concentration decreases due to the increase of their desorption rate at higher temperature.

We also find various minor products at 25% conversion of the feed 2-methylpentane, consisted of acyclic paraffins, acyclic olefins, methylcyclopentane, diolefins, cyclic olefins, and aromatics. The formation of these minor products evidence that the carbenium ions on catalyst surface undergo various sideline reactions such as elimination, ion–ion disproportionation, cyclization, aromatization and polycondensation, which gradually cause the formation of coke and catalyst deactivation.

Acknowledgments

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