JOURNAL OF CATALYSIS **141**, 148–160 (1993)

Selectivity and Yield of Components of a Composite Cracking Catalyst: Effect of Interactions between Composite Components

DADY B. DADYBURJOR[1] AND ZHENYU LIU

Department of Chemical Engineering, P.O. Box 6101, West Virginia University,
Morgantown, West Virginia 26506-6101

Received September 11, 1992; revised December 11, 1992

Coking, activity, and product distribution of a composite catalyst and its components, an REY zeolite and a silica–alumina matrix, are studied in the cracking of *n*-hexadecane at 500°C in a pulse microreactor equipped with a thermogravimetric analysis unit (TGA), an integral sample collector, and a GC. The matrix component alone does not show significant activity beyond thermal cracking. The zeolite component has high activity and high coking rate. The composite catalyst shows much higher conversion, much higher yield to C_5–C_{10}, and much lower coking rate than the values predicted from its components. The activity and the product distribution are affected by coke deposition, and this effect depends on coke level of the catalysts. Product yields for the three catalysts as functions of coke levels allow us to determine yield enhancement factors and selectivity enhancement factors (referring to the zeolite component in the composite catalyst relative to the pure zeolite catalyst at the same zeolite coke level) for four product groups. Examination of the selectivity enhancement factors indicates how the heaviest products (C_{17+}) from the matrix component of the composite catalyst convert to kerosene, gasoline, and lightest (C_{4-}) product groups over the zeolite component of the composite catalyst, and how these interconversions change with the coke level on the zeolite. © 1993 Academic Press, Inc.

INTRODUCTION

Modern cracking catalysts are usually heterogeneous complex composites of micrometer-sized zeolite in an amorphous silica–alumina matrix. Both the zeolite and the matrix have catalytic activities commonly attributed to acid sites. The zeolite is significantly more active than the matrix. Cracking selectivity and coking behavior of the two components are also different (*1–3*). Cracking on zeolite gives products rich in paraffins and aromatics, while silica–alumina favors olefins and napthenes (*4*). Composites of these two catalyst components have been reported to give product mixtures superior to either component individually, and, in some cases, exceed the sum of the component properties (*5*). However, little work has been carried out to compare actual composite catalyst performance, fresh and coked, with that of the specific components from which it was prepared. Dean and Dadyburjor (*6*) reported on the results of comparing the activity of fresh (steamed) and coked samples of composite, zeolite alone, and silica–alumina alone. The results were used to describe the flow pattern through the composite catalyst and to obtain an indirect measure of the amount of coke on each component of the composite catalyst (*6*). Selectivities of the composite and the two components are in general expected to change with deactivation level (*7*).

The main purpose of this work is to study the selectivity and yield of a composite catalyst and its components, a zeolite and an active matrix, in cracking of *n*-hexadecane as a function of coke level.

EXPERIMENT

Experiments were carried out in a pulse microreactor system, an earlier version of

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

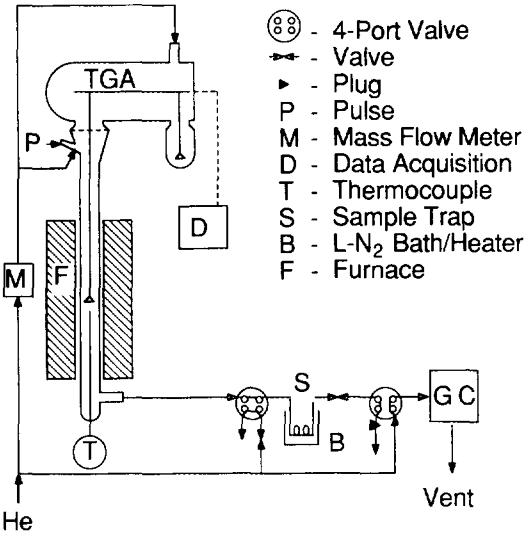

FIG. 1. Schematic of pulse microreactor.

which has been described in detail (*6*, *8*). The current version is shown in Fig. 1. The apparatus has the advantage of allowing an unambiguous determination of activity, yield, and selectivity to be made at a particular level of deactivation. The reactor is a thermogravimetric analysis (TGA) Cahn System 113. The unit is a flow-through type, with an external oven. Pulses of reactant are injected in a stream of heated helium carrier gas. The carrier gas flows over the sample of catalyst placed in a sample pan hanging in a pyrex reactor tube. Back-diffusion of the reactant to the recording and measuring head is minimized by having a separate helium stream flow through the head and through a small hole into the reactor tube. The outlet stream leaving the reactor tube flows through the sample collector, a stainless-steel U-tube of diameter 1/4″ and a total length of 11″. Condensable gases are captured in the collector at liquid-nitrogen temperatures, maintained by using a dewar. The relatively large diameter and length of the collector allows for sufficient heat transfer area with negligible pressure drop and no plugging of the tube. After a fixed amount of time, the liquid-nitrogen dewar is removed, and the contents of the collector are heated and flushed to a gas chromatograph for product analysis. A Varian 3300 GC with FID and a 10′ × 1/8″ packed column with 10% SP-2100 on 100/120 Supelcoport was used for products analysis.

The composite catalyst used is AGZ-50 from W. R. Grace and Company, which has specified the composite to contain 10–15% of REY zeolite and the balance silica–alumina matrix. The two individual components were also supplied. An unspecified mixture of rare earth oxides is used in the zeolite. The catalysts were steamed at 500°C in a fluidizing state in a vertical quartz tube for 1 h before reaction. The physical properties of the catalysts are listed in Table 1. The particle size of the steamed composite and the steamed matrix is approximately 80μm. Particle sizes of the zeolite could not be determined since the particles tended to agglomerate when sieving. The size of the loose agglomerates is approximately 150 μm. The zeolite crystallite size is approximately 1 μm. The hexadecane used was from Fisher Scientific with a purity of 99.8 mol%. The He carrier is from West Virginia Welding with a minimum purity of 99.5%.

The cracking reactions were carried out at 500°C and ambient pressure, with a overall helium rate of 90 ml/min. Approximately 5 mg of catalyst was used for each run, a weight corresponding to a negligible bed depth in the sample pan. Hence, temperature variations are expected to be negligible in the sample. The catalysts were heated under reaction conditions for 3 h before the

TABLE 1

Physical Properties of the Catalysts

	Composite	Zeolite	Matrix
Al_2O_3 (wt%)	29.0	—	35.0
Residual Na_2O (wt%)	0.23	0.88	0.50
Bulk density (g/cc)	0.62	—	0.48
Pore volume (cc/g)	0.58	—	0.66
Surface area (m^2/g)[a]	258	780	190
NH_3 chemisorption (cc/g)[a]	4.2	8.6	2.8
MAT activity (vol%)	72.0	—	34.0

[a] After steaming

reaction. The TGA balance was tared before each injection of the pulse. The pulse size was 3.87 mg, corresponding to 5 μl of liquid. The sample was collected in a liquid-nitrogen dewar for up to 2.5 min after injection of the pulse. The time interval between the pulses was 40 min. Periodically, thermal cracking experiments were also made under the same conditions, using glass beads in the place of the catalyst. Two experimental runs were made for each catalyst under the same conditions.

DATA ANALYSIS

Data analysis of the cracking experiments is based on GC areas. The weight of each component is calculated using an FID weight factor (*9*) for the component. As mentioned earlier, products were trapped at liquid nitrogen temperature, 77.4 K, for GC analysis. Although all the hydrocarbons produced in the cracking have pure-component boiling points higher than 77.4 K, a small amount will still escape from the trap because of equilibrium vapor pressure and the flow of the carrier He. Further, H_2 can not be trapped. We term all the escaped components "noncondensable-gas" (NCG). Loss of reactant to coke formation is not taken into account, since it is relatively small. The resulting numbers from the calculation are therefore on a coke- and NCG-free basis.

Products with carbon number equal to or less than 4 show only one peak in the gas chromatogram. They are treated as a single component, labeled C_{4-} in the analysis. The products with carbon number equal to or greater than 17 are also treated as a single component and are labeled C_{17+}.

RESULTS AND DISCUSSION

Coke Deposition

Coke deposition for each pulse is defined as the percentage incremental weight of the catalyst 40 min after the pulse. The relation of cumulative *n*-hexadecane to cumulative coke deposition (or coke level) is shown in Fig. 2 for the three catalysts.

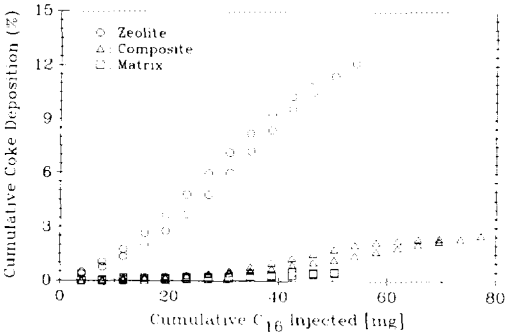

FIG. 2. Cumulative coke deposition as a function of cumulative hexadecane injected over each of three catalysts. Circles, pure zeolite; squares, pure matrix; triangles, composite.

The rate of coke deposition is the highest for the REY zeolite and the lowest for the matrix. A sigmoidal shape can be seen for both the zeolite and composite catalyst; coke levels are too low for such behavior to be observed for the matrix. The maximum incremental coke deposition (MICD), corresponding to the maximum coking rates for the zeolite and the composite, are at 7 and 1.2% coke, respectively. The shape of the coking curve suggests that autocatalytic coking plays an important role in the coking kinetics. The phenomenon has been reported by us for other catalysts and reactants as well (*10*).

Deposition of coke on the composite catalyst tends towards a plateau, at a coke level of approximately 2.6%. This corresponds to a value of the Maximum Coke Deposition (MCD) of 2.6% for the composite, consistent with Ref. (*10*). For the zeolite, a plateau is not observed, at least in the experimental time period. However, the model of Ref. (*10*) allows us to estimate the MCD value for the zeolite as approximately 18%. The MCD for the matrix cannot be estimated, as the coke levels in the current experiment are too low.

It is important to note that the autocatalytic coking behavior indicates that using time or cumulative reactant as the independent variable for conversion and selectivity

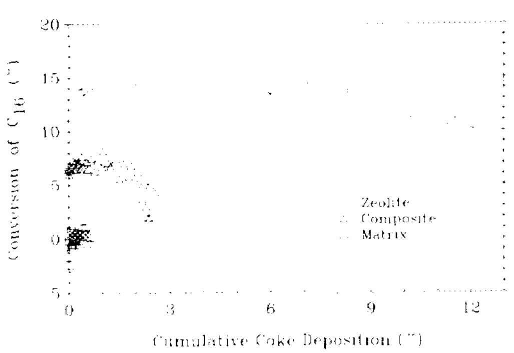

FIG. 3. Incremental conversion of hexadecane as a function of cumulative coke deposition on each of three catalysts. Conversion values have been adjusted to correspond to a (fresh) catalyst weight of 5.00 mg. The results of thermal (noncatalytic) runs have been subtracted. Symbols are those used in Fig. 2.

analysis is inappropriate, because different amount of cumulative reactant may give the same amount of coke when the maximum coke deposition is reached. The cumulative coke deposition, therefore, is used as the independent variable in the following analysis.

Activity

The activity is defined here as the observed percentage of n-hexadecane reacted, less that reacted by thermal cracking. Activities of the three catalysts are plotted versus the cumulative coke deposition in Fig. 3. The zeolite gives the highest activity and the matrix has no significant activity under the experimental conditions.

The composite, which contains 10–15% of zeolite, shows an initial activity about 50% of that of the pure zeolite. There is clearly an enhanced reaction for zeolites in the composite catalyst, perhaps due to the smaller size of the zeolite in the composite, relative to the pure component. This is quantified later. The effect cannot be explained by the reduced coking rate, since for the fresh catalyst, the coke deposition is negligible. Further, the activity of the composite does not decrease with coke levels up to approximately 2%, greater than levels found in commercial practice. For the zeolite and composite, the activities are more or less constant before the maximum coking rate is reached. The activity then starts to decrease with increasing rates. When the MCD value is reached for the composite catalyst, the activity approaches zero. This suggests that the maximum coking rate can be used as a parameter to define the availability of the acid sites used in the cracking reaction. We have discussed such a model earlier (*10*, *11*).

Product Distribution

Products of C_{4-}, C_5–C_{15}, and C_{17+} were observed in the GC analysis. The amount of NCG formed (and then escaping from the collector) for one catalyst is different from that for another. Hence yield, which is defined here as the amount of a product formed relative to the total sample collected ($wt_{Ci}/\Sigma wt_{Ci}$), is a useful measure of the catalyst performance. The product distributions, in terms of yield, at several coke levels are plotted in Figs. 4, 5, and 6 for the matrix, zeolite, and composite, respectively. The amounts of products formed from thermal cracking have already been subtracted.

The product distribution for the matrix is affected by coke level and is close to that of thermal cracking. For the fresh matrix,

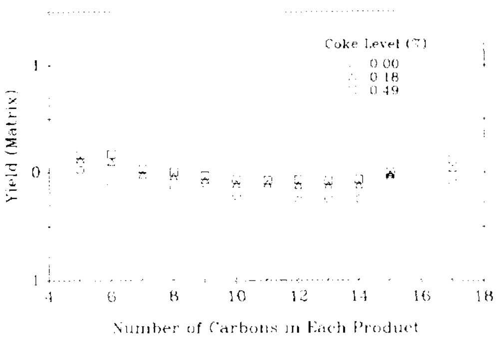

FIG. 4. Effect of coke level on the product yield (by carbon number) over pure matrix catalyst. For clarity, only three coke levels are shown. Yield values have been adjusted to correspond to a (fresh) catalyst weight of 5.00 mg.

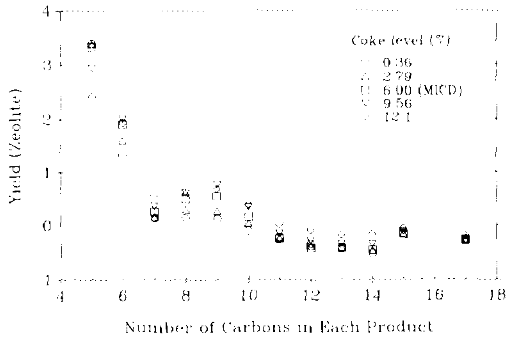

FIG. 5. Effect of coke level on the product yield (by carbon number) over pure zeolite catalyst. For clarity, only five coke levels are shown. Note that the squares represent data near the maximum coking rate for the zeolite. Yield values correspond to a (fresh) catalyst weight of 5.00 mg.

the yields of C_6 to C_{17+} are all smaller than those for thermal cracking. As coke level increases, the yields increase. The yield of a lighter product is generally higher than that of a heavier product, except for C_{15} and C_{17+}.

The product distribution for the zeolite is different from that of the matrix. More of the lighter products are formed, especially for C_5 and C_6. For the fresh zeolite, the yields of C_5 and C_6 are much higher than those of other products. This may be related to the high acidity of the REY zeolite and to secondary cracking. As coke level increases, the yield to C_5 decreases slowly until the MICD is reached, after which the yield decreases sharply. For products in the C_{11}–C_{14} range, their yields increase with an increase of coke level, slowly at first, and then rapidly after the MICD. These mirror relations between the C_5-and-lighter and C_{11}–C_{14} fractions may indicate that the acid site density is greatly reduced at this coke level, and results in less secondary cracking. The dependence of the yields for C_6–C_{10} products on coke level are intermediate between the C_{5-} and the C_{11}–C_{14} products.

The dependence of the product distribution on the coke level for the composite catalyst (Fig. 6) is similar to that for the zeolite. Moreover, at high coke levels, the relation between coke and yield for C_6, C_7, and C_8 become different from those at lower coke levels. The yields of these products increase with an increase of coke level initially, but decrease when the coke level approaches the maximum value. The transition apparently starts after the maximum coking rate occurs. At high coke levels, the yields to all products approach those of thermal cracking. This indicates that almost all of the acid sites are lost at the maximum cumulative coke level. This behavior can also be seen for the zeolite (in Fig. 5), for C_6, for example.

Quantitative Model for Activity

This subsection and the next builds upon the work of Dean and Dadyburjor (*6*). The idea there was to use activity- and coke-vs-injection data for the two individual components and the composite catalyst to determine the simplest model of flow through the (coked) composite. This model can be used to quantify the incremental selectivity changes associated with combining the two components into the composite catalyst. The simplest flow model that could explain the activity and coke data within the experimental error bounds was found to be the so-called partitioned-flow model. This is illus-

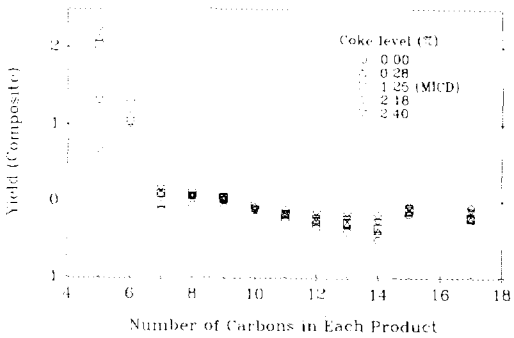

FIG. 6. Effect of coke level on the product yield (by carbon number) over the composite catalyst. For clarity, only five coke levels are shown. The squares represent data at the maximum coking rate for the composite. Yield values correspond to a (fresh) catalyst weight of 5.00 mg.

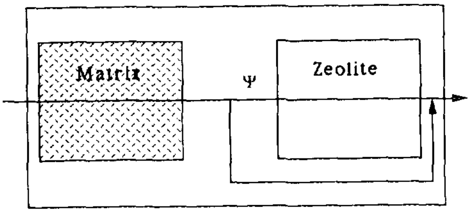

FIG. 7. Schematic of the partitioned-flow model, based on Ref. (6).

trated in Fig. 7. Here all the reactant enters the matrix and a portion is reacted, depending upon the matrix coke level. The resulting stream is partitioned, with a fraction ψ passing through the zeolite and the remainder $(1 - \psi)$ bypassing the zeolite. The zeolite fraction ψ can be obtained as a function of coke level, by carrying out a coke balance. The coke levels on the individual components of the composite can be also obtained from this model.

Due to the improvements in the present apparatus, the experimental error bars are now much reduced, and a more detailed model is possible to characterize the flow through the coked composite. The modified model builds on the old partitioned-flow model and is described below. In brief, the new model accounts for the enhanced reactivity of the zeolite component in the composite by introducing an enhancement factor α (relative to the pure zeolite component) as well as the zeolite faction ψ. The new model is then used in the next subsection to quantify the changes in selectivity of the composite with coke level.

The level of coke on a pure component or composite, C_j, where j = z, m, or c representing pure zeolite, pure matrix, or composite, respectively, is a function of $v_{j,in}$, the cumulative amount of reactant hexadecane injected per unit weight of catalyst,

$$v_{j,\mathrm{in}} = V_{j,\mathrm{in}}/w_j \qquad (1a)$$

$$C_j = C_j(v_{j,\mathrm{in}}). \qquad (1b)$$

Since all the reactant injected over the composite passes over the matrix component, the coke level on the matrix component of the composite, $C_{\mathrm{m,c}}$, is equal to the coke level on the pure matrix component corresponding to the appropriate value of v_m:

$$C_{m.c} = C_m(v_m = V_{c,in}/\{\varepsilon_m w_c\}). \qquad (2)$$

Here ε_m is the weight fraction of the matrix in the composite catalyst. $C_{\mathrm{m}}(v_{\mathrm{m}})$ can be obtained from experimental data for the pure matrix catalyst in Fig. 2. Then a coke balance allows us to obtain $C_{z,c}$, the coke level on the zeolite component of the composite catalyst,

$$C_{z,c} = \{C_c(v_{c,\mathrm{in}}) - \varepsilon_{\mathrm{m}} C_{\mathrm{m,c}}\}/\varepsilon_z, \qquad (3)$$

where ε_z is the weight fraction of the zeolite in the composite catalyst. $C_c(v_{\mathrm{in}})$ can be obtained from experimental data for the composite catalyst in Fig. 2.

Figure 8 represents the coke levels on the matrix component and the zeolite component of the composite catalyst, as functions of the (overall) coke level on the composite catalyst. The relations correspond to equation (2) and (3) with

$$\varepsilon_z = 0.11 \qquad (4a)$$

$$\varepsilon_{\mathrm{m}} = 0.89 \qquad (4b)$$

as discussed earlier. The figure indicates that there is an initial period in which the matrix coke level is higher than the zeolite coke level, perhaps because little of the re-

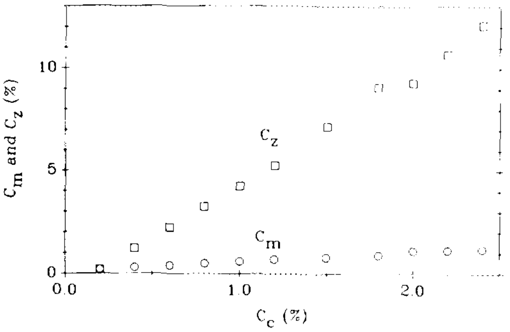

FIG. 8. Coke levels on the zeolite and matrix components of the composite as a function of the coke level on the composite, based on the partitioned-flow model.

actant has passed over the zeolite at this point. After this initial period, the zeolite component has a higher level of coke. Qualitatively similar results were obtained by Dean and Dadyburjor (6).

The calculated coke level on the zeolite component allows us to estimate the reactant entering that component of the composite catalyst, $V_{z,c,in}$, using the inverse of Eq. (1b):

$$v_{z,c,in} = v_z(C_z = C_{z,c}). \qquad (5a)$$

Experimental data on the pure zeolite component allows $v_z(C_z)$ to be obtained. Then

$$V_{z,c,in} = \varepsilon_z w_c v_{z,c,in}. \qquad (5b)$$

From Eq. (5b), the incremental amount of reactant entering the zeolite component of the composite catalyst in a particular pulse, $\Delta V_{z,c,in}$, can be obtained.

The fractional conversion per unit weight of catalyst

$$x_j = X_j/w_j \qquad (6a)$$

is a function of the corresponding coke level, C_j. Then the conversion $X_{m,c}$, ascribed to the matrix component of the composite catalyst, can be written in terms of the corresponding coke level, $C_{m,c}$, as

$$X_{m,c} = \varepsilon_m w_c \cdot x_m(C_m = C_{m,c}). \qquad (6b)$$

Here $x_m(C_m)$ can be obtained from experimental data on the pure matrix component; see Fig. 3. Then the incremental amount of reactant leaving the matrix component of the composite catalyst for a particular pulse is

$$\Delta V_{m,c,out} = \Delta V_{c,in}\{1 - X_{m,c}\}, \qquad (7a)$$

where $\Delta V_{c,in}$ is the incremental reactant entering the (matrix component of the) composite. Equation (7a) allows the calculation of the incremental amount of reactant bypassing the zeolite in a particular pulse:

$$\Delta V_{byp} = \Delta V_{m,c,out} - \Delta V_{z,c,in}. \qquad (7b)$$

Therefore the incremental bypass fraction $(1 - \psi)$ is

$$1 - \psi = \Delta V_{byp}/\Delta V_{m,c,out}. \qquad (7c)$$

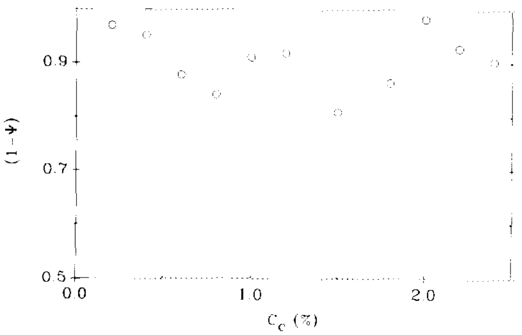

FIG. 9. Incremental bypass fraction for the deactivating composite catalyst.

The calculated values of the incremental bypass fraction, $(1 - \psi)$, are shown in Fig. 9 as a function of the deactivation of the catalyst, quantified by the overall coke level on the composite. The relative amounts of zeolite and matrix in the composite catalyst are given by Eq. (4), consistent with Fig. 8. The values of $(1 - \psi)$, are high, indicating that relatively little of the reactant passes over the zeolite component. The values decrease initially with increasing coke level, indicating that paths involving the zeolite are made more favorable by coke deposition on the matrix. However, the values of $(1 - \psi)$ pass through a minimum and then increase again, perhaps as increasing amounts of coke deposit on the zeolite. Note that the minimum occurs at a composite coke level around 1.5–2%, higher than the value at the end of a typical commercial riser reactor.

The previous model (6) assumed that the zeolite conversion in the composite could be obtained from the pure zeolite data. However, in the present case, this leads to the predicted conversion for the composite catalyst being very much smaller than the experimental values obtained, and the difference is greater than the experimental error expected. The present model ascribes the enhanced reaction to the zeolite component only. For the fresh catalyst, the enhancement may be due to the absence of diffusion effects for the smaller particles of zeolite in the composite, relative to the size

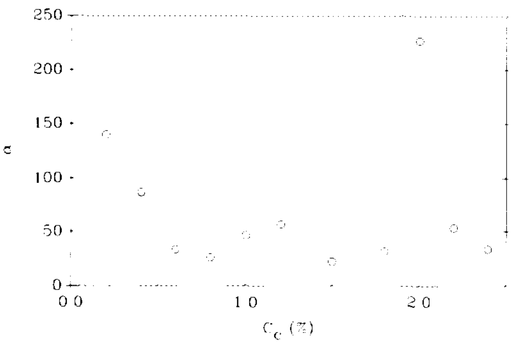

FIG. 10. Activity enhancement factor for the deactivating composite catalyst.

of the pure zeolite catalyst. For the coked catalyst, the enhancement could be different from that of the fresh catalyst, depending upon the relative diffusion effects in the matrix and zeolite components.

Then the conversion in the zeolite component of the composite catalyst, $X_{z,c}$, can be related to that expected in the pure component per unit weight of zeolite, $x_z(C_z)$, by

$$X_{z,c} = \alpha \varepsilon_z w_c x_z(C_z = C_{z,c}), \quad (8)$$

where α is the activity enhancement factor. The overall conversion in the composite for a particular pulse is given by

$$X_c = \{\Delta V_{c,\mathrm{in}} - \Delta V_{c,\mathrm{out}}\}/\Delta V_{c,\mathrm{in}}, \quad (9a)$$

where $\Delta V_{c,\mathrm{out}}$ is the incremental reactant leaving the composite, given by

$$\Delta V_{c,\mathrm{out}} = \Delta V_{\mathrm{byp}} + \Delta V_{z,c,\mathrm{out}}, \quad (9b)$$

and where the incremental reactant leaving the zeolite component of the composite is

$$\Delta V_{z,c,\mathrm{out}} = \Delta V_{z,c,\mathrm{in}}\{1 - X_{z,c}\}. \quad (9c)$$

Hence the activity enhancement factor, α, can be obtained from Eqs. (8) and (9) as

$$\alpha = \{\Delta V_{c,\mathrm{in}}/\Delta V_{z,c,\mathrm{in}}\}\{x_c(C_c) - \varepsilon_m x_m(C_m = C_{m,c})\}/\{\varepsilon_z x_z(C_z = C_{z,c})\}. \quad (10)$$

Figure 10 illustrates the changes in α with a deactivating catalyst. The relative amounts of zeolite and matrix used are those used earlier, in equation (4). Initial values of α are of the order of 100, equivalent to the size ratio of zeolite component and the overall composite. This value of α is therefore consistent with activity improvements expected if the zeolite particle size is decreased and if the zeolite activity is diffusion-limited. The activity enhancement decreases rapidly with increasing amount of coke on the composite, and appears to level off at coke values greater than approximately 1.5%.

It is important to note that Figs. 8–10 represent the results of only a simple quantitative model. A major assumption here is that the presence of the zeolite has no effect on the matrix coke and activity. In fact, reactants and products leaving the zeolite must pass through the matrix, and could alter its coking characteristics. Further, the enhanced activity of the zeolite in the composite could be due to zeolite–matrix interactions, as well as to diffusion effects, as has been suggested here. These additional factors could be included in a more complicated model, for example, one incorporating a matrix element after the zeolite as well as before. We believe that it is better to use the simplest possible model and to use the quantitative parameters therefrom (ψ, α) as descriptors of the process rather than as absolute physical indicators.

Qualitative Model for Selectivity

In order to obtain the effects of increasing coke level, the data of Figs. 4–6 are reformulated to show the yields of C_{4-}, C_{5-10}, C_{11-15}, and C_{17+} as a function of coke level in Figs. 11–14, respectively. In each figure, the yields are shown over pure zeolite, pure matrix, and the composite catalyst. The quantitative model developed in this section allows us to compare the yield of each product group over the composite catalyst with the yield expected over the pure matrix and the pure zeolite, with each catalyst component being characterized by its own individual coke level, rather than the overall coke level of the composite catalyst.

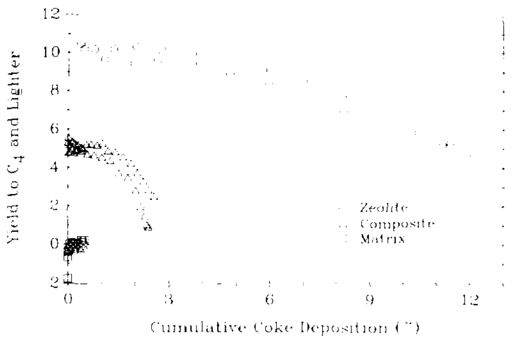

FIG. 11. Yield of the lightest product group (l, C_{4-}) obtained over 5.00 mg of each of the three catalysts. Circles, pure zeolite; squares, pure matrix; triangles, composite.

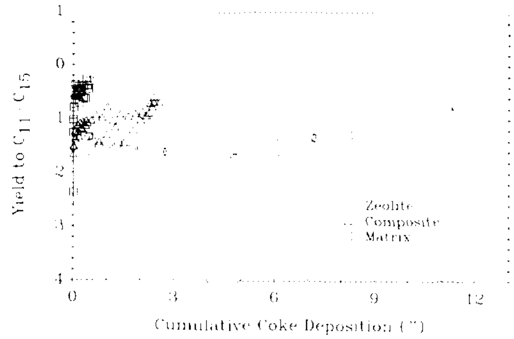

FIG. 13. Yield of the kerosene-range product group (k, C_{11-15}) obtained over 5.00 mg of each of the three catalysts. Symbols are as in Fig. 11.

For product group p, the yield over catalyst j depends upon the weight of catalyst, w_j, and the coke level C_j. Then

$$Y_{p,j} = y_{p,j}(C_j) \cdot w_j. \qquad (11)$$

Here p = l, g, k, or h for groups C_{4-} (light), C_{5-10} (gasoline, (*12*)), C_{11-15} (kerosene, (*12*)), and C_{17+} (heavy), and j = z, m, or c as before. The yield $Y_{p,j}$ is defined from

$$\Delta W_{p,j,\mathrm{out}} = \Delta V_{j,\mathrm{in}} Y_{p,j}, \qquad (12)$$

where $\Delta W_{p,j,\mathrm{out}}$ is the incremental amount of product group p leaving catalyst j. For the composite catalyst, the partitioned-flow model postulates that the product stream has two constituents, one bypassing the zeolite (and thus being characteristic of the matrix alone) and the other passing over the zeolite after passing over the matrix. It is reasonable to assume that the composition of the stream bypassing the zeolite is identical to that entering the zeolite component; in other words, only the flow is partitioned, not the composition. Then, for the composite catalyst

$$\Delta W_{p,\mathrm{c,out}} = \Delta W_{p,\mathrm{z,c,out}} + (1 - \psi)\, \Delta W_{p,\mathrm{m,c,out}}, \qquad (13)$$

where, as before, subscripts (z, c) and (m, c) denote components zeolite and matrix, respectively, of the composite catalyst.

The product yield from the matrix component of the composite catalyst is postulated to be the same (per unit weight of matrix)

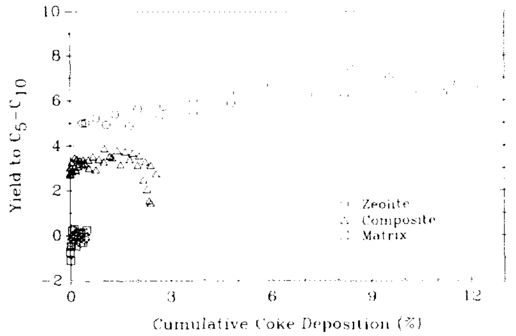

FIG. 12. Yield of the gasoline-range product group (g, C_{5-10}) obtained over 5.00 mg of each of the three catalysts. Symbols are as in Fig. 11.

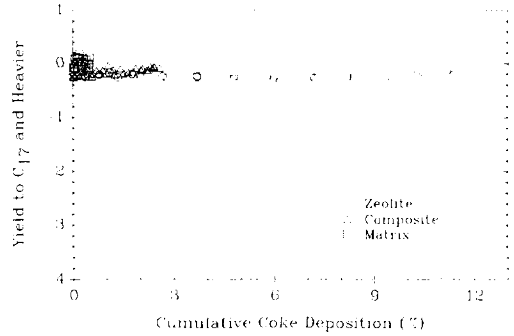

FIG. 14. Yield of the heaviest product group (h, C_{17+}) obtained over each of the three catalysts. Symbols are as in Fig. 11.

as that from the pure matrix component at the same matrix coke level. Changes in the product yield of the composite (relative to the pure component catalysts) are quantified by means of a yield enhancement factor, γ_p, associated with (unit weight of) the zeolite component, relative to the yield expected for the pure zeolite component (per unit weight) at the same zeolite coke level. This is consistent with the use of the activity enhancement factor α in the previous subsection. Then

$$\Delta W_{p,\mathrm{m,c,out}} = \Delta V_{\mathrm{c,in}}\varepsilon_{\mathrm{m}} w_{\mathrm{c}} \, y_{p,\mathrm{m}}(C_{\mathrm{m}} = C_{\mathrm{m,c}}) \quad (14)$$

where $y_{p,\mathrm{m}}$, the yield of product p per unit weight of the matrix, can be obtained as a function of the pure matrix coke level, C_{m}, from Figs. 11–14. Further,

$$\Delta W_{p,\mathrm{z,c,out}} = \Delta V_{\mathrm{z,c,in}}\varepsilon_{\mathrm{z}} w_{\mathrm{c}} \, y_{p,\mathrm{z}}(C_{\mathrm{z}} = C_{\mathrm{z,c}}) \cdot \gamma_p, \quad (15)$$

where $y_{p,\mathrm{z}}$ is the analog of $y_{p,\mathrm{m}}$ for a pure zeolite catalyst. From Eqs. (12)–(15), γ_p can be obtained as

$$\gamma_p = \{\Delta V_{\mathrm{c,in}}/\Delta V_{\mathrm{z,c,in}}\}\{y_{p,\mathrm{c}}(C_{\mathrm{c}}) - \{1 - \psi\}\varepsilon_{\mathrm{m}} y_{p,\mathrm{m}}(C_{\mathrm{m}} = C_{\mathrm{m,c}})\}/\{\varepsilon_{\mathrm{z}} y_{p,\mathrm{z}}(C_{\mathrm{z}} = C_{\mathrm{z,c}})\}. \quad (16)$$

The enhancement of the yield of a particular product has two factors. One of these is the increased reaction rate in the zeolite component of the composite catalyst due to the smaller size relative to the pure zeolite catalyst. The second factor is the selectivity improvement expected over the zeolite component in the composite since the inlet of the zeolite component contains matrix-cracked products rather than only reactant hexadecane. The first factor has been quantified as α. Hence a selectivity enhancement factor, σ_p, may be defined for each product p from

$$\gamma_p = \alpha\sigma_p. \quad (17)$$

Values of σ_p for each product group are shown in Fig. 15.

The selectivity enhancement for the light products, C_{4-}, is approximately unity at all coke levels, except perhaps at the highest. This implies that the increased yield of these products can be ascribed only to the increased zeolite activity. For the heaviest products, C_{17+}, the yields are small over all three fresh catalysts, and are difficult to evaluate at the higher coke levels. The σ_{h} values at the lower coke levels appear to increase with increasing coke. In other words, the selectivity for the heaviest products increases for the deactivating catalyst. Further, the values of σ_{h} are less than unity. This means that (zeolite) selectivity for these products is less when the zeolite is a component of the composite catalyst than when the zeolite alone is used as the catalyst, the zeolite in both cases having the same coke level.

The σ values for the gasoline fraction and the kerosene fraction are generally greater than unity. For the fresh catalyst, σ_{g} and σ_{k} are approximately equal in value, approximately 1.5. This means that the (zeolite) selectivity is approximately 50% better for the zeolite as a component of the composite catalyst, relative to the pure zeolite. As the catalyst deactivates, the σ_{k} values decrease more than σ_{g} values, reach a minimum (approximately 0.8), and then increase. The σ_{g} values exhibit a shallow minimum (approximately unity), at much higher values of the coke level. Hence the gasoline selectivity of the fresh zeolite in the composite catalyst is enhanced (relative to the pure zeolite catalyst), but the enhancement decreases with increasing coke on the zeolite. The kerosene selectivity enhancement decreases rapidly with increasing zeolite coke, but then increases. The increase in enhancement appears to be at the expense of the gasoline enhancement.

Figure 16 illustrates the overall process. Hexadecane passing over the zeolite (alone), in the top of the figure, cracks with C_{4-}, C_{5-10}, and C_{11-15} products and con-

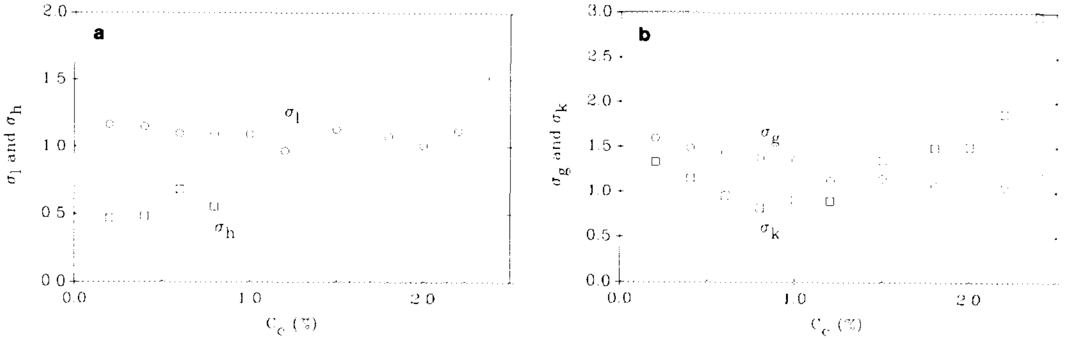

FIG. 15. Selectivity enhancement factors for the four product groups as a function of the coke level of the deactivating composite catalyst.

denses into heavier, C_{17+} products. Similarly, hexadecane passing over the matrix, in the center of the figure, forms cracking and condensation products, but with selectivities different from those characteristic of the matrix. Since hexadecane passing over the composite catalyst is assumed to pass over the matrix component first, the products over the matrix component in the composite are expected to be the same as those over the matrix alone. Unreacted hexadecane from the matrix component of the composite catalyst, when passing over the zeolite component of the composite catalyst, reacts to form products with the same selectivity as over the zeolite (alone) at the same zeolite coke level. These products are shown by the arrows at the top of the block in the bottom of Fig. 16.

In addition, the products from the matrix component (viz., C_{4-}, C_{5-9}, C_{10-15}, and C_{17+}) react further in the zeolite component. For clarity, arrows to only adjacent products are shown in the bottom block (e.g., C_{11-15} to C_{5-10} and C_{17+}) although the compounds can form other products as well (e.g., C_{11-15} to C_{4-}). Also, products from the thermal (non-catalytic) reactions are not shown in Fig. 16.

Figure 16 can be used to understand the quantitative results of Fig. 15. For the fresh catalyst, for which $\sigma_l = 1.2$, $\sigma_g = 1.6$, $\sigma_k = 1.3$, and $\sigma_h = 0.5$, the net action of the zeolite is to convert the C_{17+} products to the C_{5-10} range, to a somewhat lesser extent to the C_{10-15} range, and to a small extent to the C_{4-} range. As the catalyst deactivates (to about 0.8 percent coke on the composite, approximately 3% on the zeolite), σ_h increases, σ_k decreases, σ_g decreases but to a smaller extent, and σ_l decreases slightly. Hence the 3%-coked zeolite converts less of the heaviest products to the C_{11-15} range, although the interconversion to the C_{5-10} range and to the lightest products decrease to a smaller extent. Recall that this coke level is less than that corresponding to the maximum coking rate (the MICD). At higher coke levels (1.5% on the composite, 7% on the zeolite component), σ_k increases, σ_g decreases (to approximately unity), and σ_l decreases slightly. The net change in the C_{5-10} selectivity (relative to the pure zeolite) is negligible, i.e., there is now a net change of the heaviest products to the C_{11-15} range. Alternatively, as much C_{5-10} is converted to C_{11-15} as C_{17+} is converted to C_{5-10}. At these highest coke levels, higher than those corresponding to the maximum coking rate, virtually all of the heaviest products are reacted away, even those formed from thermal (non-catalytic) reactions.

CONCLUSION

Coking and other catalytic behavior (activity, selectivity, and yield) for a composite cracking catalyst and its components, zeolite and matrix, are studied for the cracking

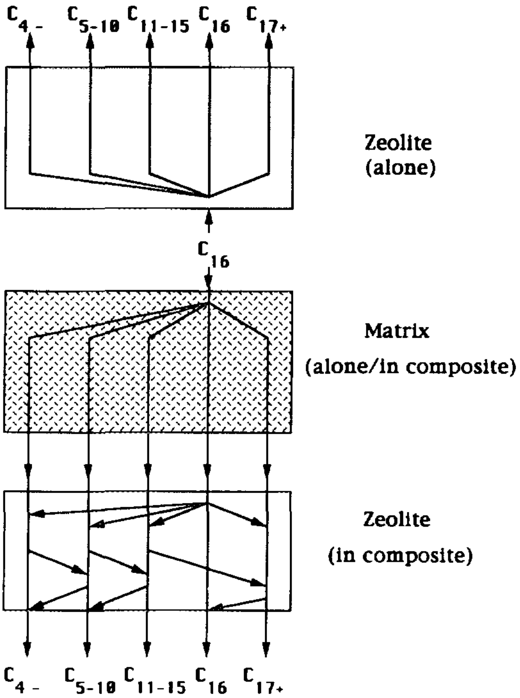

FIG. 16. Schematic of the conversion of hexadecane (C_{16}) to the four product groups over the pure zeolite catalyst (top compartment); matrix, pure and as a component of the composite catalyst (middle compartment); and the zeolite as a component of the composite catalyst (bottom compartment). Note that the feed into the zeolite component of the composite consists of C_{16} as well as the four product groups from the matrix component. The bypass fraction is not explicitly shown in the figure.

of *n*-hexadecane in a pulse microreactor with integral sample collection and on-line gas chromatography. The apparatus allows the catalytic behavior to be studied at well-defined coke levels.

The coking for the zeolite and the composite shows autocatalytic behavior. The maximum coke levels for the zeolite and composite correspond to individual coke levels of 18 and 2.6%, respectively. Coke levels on the matrix are very low.

The matrix component itself does not show significant activity beyond thermal cracking. The product distribution for the matrix is also not very much different from that of thermal cracking. The yield for the collected compounds increases with an increase of coke level. The zeolite component, on the other hand, has a high activity and high coking rate.

The maximum coking rate is an important parameter in distinguishing conversion and product distribution patterns. Before the maximum coking rate is reached, the conversion and the yield to the kerosene fraction (k, C_{11-15}) are constant, but the yield to the gasoline fraction (g, C_{5-10}) increases, and the yield to the lightest fraction (l, C_{4-}) decreases as the coke level increases. After the maximum coking rate is observed, however, the yield to l and g decrease, while that to k increases, with an increase of coke level. The maximum yield to g is at the coke level where the maximum coking rate occurs.

The activity of the composite was analyzed in terms of the pure component values using the partitioned-flow model. The corresponding coke balance indicates that coking rates for the fresh composite catalyst are greater over the matrix component than the zeolite component; however, after approximately 0.2% coke level, the coke deposits preferentially over the zeolite component. For the composite, a relatively large fraction of the material leaving the matrix bypasses the zeolite; the bypass fraction $(1 - \psi)$ decreases slightly as the matrix cokes, then increases again as zeolite coke levels increase. The zeolite activity in the fresh composite is much greater than that of the pure zeolite at the same zeolite coke level, probably due to the smaller size. This activity enhancement, α, decreases as the coke level increases.

Yield enhancements and selectivity enhancements for the four product groups are similarly defined. In each case, the comparison of the pure zeolite catalyst is with the zeolite component of the composite having the same zeolite coke level, not the same composite (overall) coke level. Selectivity enhancement factors σ_g and σ_k are greater than unity for the fresh catalyst, and pass through a minimum with increasing coke level. For l, the parameter stays around unity and passes through a shallow minimum. The parameter σ_h is much smaller than unity and increases with coke level. Physically, these trends indicate that the zeolite component in the fresh composite converts products h from the matrix component to products l, g, and k. At zeolite coke levels less than that corresponding to the maximum coking rate of the zeolite component, less h is converted to k. At zeolite coke levels greater than that corresponding to the maximum coking rate of the zeolite component, more h is converted, and more of it is converted to k.

The present experimental technique and data manipulation allow us to obtain the details of the effect of coke on the activity and selectivity of the components of the composite cracking catalyst. Hence the procedure can be used to determine the effect of zeolite and matrix properties on the performance of the composite catalyst.

APPENDIX: NOMENCLATURE

C_j	Coke percent on catalyst j (%)
v_j	Cumulative reactant per unit weight of catalyst j (mg)/(mg)
V_j	Cumulative reactant over catalyst j (mg)
ΔV_j	Incremental reactant (mg)
w_j	Weight of catalyst j (mg)
$\Delta W_{p,j}$	Increment product p formed over catalyst j (mg)
x_j	Fractional conversion of reactant per unit weight of catalyst j (%)/(mg)
X_j	Fractional conversion of reactant over catalyst j (%)
$y_{p,j}$	Yield of product p per unit weight of catalyst j (%)/(mg)
$Y_{p,j}$	Yield of product p over catalyst j (%)

Greek

α	Activity enhancement factor, zeolite in composite compared to pure zeolite
γ_p	Yield enhancement factor for product group p
ε_j	Weight fraction of j = m, z in composite catalyst
σ_p	Selectivity enhancement factor for product group p
ψ	Zeolite fraction of flow

Subscripts

c	Composite catalyst
g	Gasoline-range product group, C_{5-10}
h	Heaviest product group, C_{17+}
in	Entering the catalyst (pure, composite, or component)
k	Kerosene-range product group, C_{10-15}
l	Lightest product group, C_{4-}
m	Matrix
m,c	Matrix component of composite catalyst
out	Leaving the catalyst (pure, composite, or component)
z	Zeolite
z,c	Zeolite component of composite catalyst

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance of Dr. K. Rajagopalan, W. R. Grace and Co., with the samples and their characterization. Zhang Zhenru carried out some of the earlier experimental runs. This work was supported by the Exxon Educational Foundation.

REFERENCES

1. Plank, C. J., Rosinski, E. J., and Hawthrone, W. P., *Ind. Eng. Chem. Prod. Res. Dev.* **3**, 165 (1964).
2. Nace, D. M., *Ind. Eng. Chem. Prod. Res. Dev.* **8**, 24 (1969).
3. Weisz, P. B., *Chemtech.* **3**, 498 (1973).
4. Weisz, P. B., *Annu. Rev. Phys. Chem.* **21**, 175 (1970).
5. Oblad, A. G., *Oil Gas J.* **70**, (13), 84 (1972).
6. Dean, J. W., and Dadyburjor, D. B., *Ind. Eng. Chem. Res.* **27**, 1754 (1988); **28**, 271 (1989).
7. Dadyburjor, D. B., *in* "Catalysis, Vol. 9," (J. J. Spivey, Ed.), p. 229. Royal Society of Chemistry, London, 1992.
8. Dadyburjor, D. B., and Dean, J. W., *AIChE J.* **33**, 1829 (1987).
9. Kaiser, R., *Gas Chromatogr.* **3**, 99 (1963).
10. Liu, Z., and Dadyburjor, D. B., *J. Catal.* **134**, 583 (1992).
11. Dadyburjor, D. B., and Liu, Z., *Chem. Eng. Sci.* **47**, 645 (1992).
12. Satterfield, C. N., "Heterogeneous Catalysts in Practice." McGraw-Hill, New York, 1980.