Relative reactivities of alkanes in multi-component catalytic cracking reactions

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An experimental technique is discussed for measuring relative reactivities of alkanes in the catalytic cracking of multi-component hydrocarbon mixtures over a heterogeneous, Y-zeolite-based catalyst at 250–350°C. With the technique, ca. 0.1 μl of an alkane mixture is evaporated and contacted with a catalyst, after which the mixture of reaction products and the unreacted feed enters the chromatographic column and is immediately analyzed. The technique is used to measure relative reactivities of 21 alkanes in a single experiment. The principal results of these experiments are similar to the results of single-component cracking: alkane reactivity rapidly increases with the increase of the carbon number, and methyl-branched alkanes are more reactive than linear alkanes. However, the variations in alkane reactivities as a function of their molecular weight and skeleton structure differ very significantly between single- and multi-component experiments.

Keywords: Catalytic cracking; alkane cracking; isoalkane cracking; alkane reactivities in catalytic cracking

1. Introduction

Information on relative reactivities of alkanes in cracking reactions over solid acidic catalysts plays an important role in our understanding of this complex process. A significant amount of data on this subject has already been accumulated. It was discovered a considerable time ago that alkane reactivities strongly depend on the types and the number of various C–H bonds in their molecules [1–3] and that the relative C–H bond reactivities in CH, CH_2 and CH_3 groups decrease approximately as 20 : 2 : 1 [3]. Archibald et al. [4], Flinn et al. [5] and Nace [6] reported that *n*-alkane reactivity increases with the increase of the carbon number. This conclusion was later confirmed in a detailed kinetic study of Abbot and Wojciechowski [7].

Recently we described a simple technique for the measurement of the relative

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alkane reactivities in the cracking reactions in the 250–400°C range [8]. Reactivities of ca. 50 C_8–C_{17} alkanes were evaluated. These measurements confirmed that the principal factors affecting alkane reactivities are their molecular weights and the type, number and position of substituents. The present article describes an extension of this technique to the reactivity measurements for a large number of alkanes in the course of a single multicomponent cracking experiment.

2. Experimental

As was described previously [8], a gas chromatograph was used both as a cracking reactor and as an analytical tool. The catalyst was a commercial steam-equilibrated cracking catalyst FSS-1 (Filtrol). It contained ca. 20% of the rare earth-exchanged Y zeolite with S_0 of 400–500 m^2/g. A small load of the catalyst (0.026 g) was placed in the injection assembly of the chromatograph and dried in a He flow at 200°C. To carry out a cracking reaction, the injection assembly was heated to 250 or 350°C, and 0.1 µl of a feed mixture containing 21 alkanes dissolved in n-C_6 was injected in the space above the catalyst. The feed contained linear alkanes from n-C_7 to n-C_{20} and 2-methyl-branched alkanes from 2-Me-C_7 to 2-Me-C_{18}, each at ca. 4 wt% concentration in the mixture. At these feed/catalyst ratios, each alkane molecule has ca. 1000 $Å^2$ of the zeolite surface available for adsorption and reaction.

The feed evaporated and produced a gas mixture containing ca. 0.1 mmol of hydrocarbon vapor per liter of He. The vapor contacted the catalyst over a period of ca. 1 s and then the mixture of the unreacted feed and reaction products immediately entered an chromatographic column. A Hewlett-Packard 5880A gas chromatograph was equipped with a 50 m, 0.2 mm i.d. column coated with the 0.5 film of cross-linked methyl silicone. The He flow rate was 1 cm^3/ min, and the column temperature increased from 40 to 300°C at a rate of 5°C/ min.

3. Kinetic treatment of experimental data

The gas chromatogram of an alkane mixture cracked under mild conditions consists of the peaks of unreacted components and those of numerous cracked products, light alkanes and olefins [9]. Evaluation of the reaction conversion for each component A_i in such a mixture requires the use of an internal standard, a compound which is not affected by the catalyst. The search of possible internal standards in separate cracking experiments showed that neither light linear alkanes nor aromatic compounds are suitable for the purpose: the alkanes react with the catalysts and aromatic compounds are alkylated by olefinic products. The compound which was found best suitable as the internal standard is methylcyclopentane: its relative concentrations in the mixtures remained practically unaffected by the reaction.

To calculate conversion C_i in a cracking reaction, four peak areas (PA) were compared: those of methylcyclopentane in the reaction products and in the conventional chromatogram of the feed mixture ($\mathrm{PA}_{\mathrm{MeCP}}$ and $\mathrm{PA}^0_{\mathrm{MeCP}}$), and the peak areas on each alkane in the same two chromatograms (PA_i and PA^0_i). The $R_0 = \mathrm{PA}^0_i/\mathrm{PA}^0_{\mathrm{MeCP}}$ and $R = \mathrm{PA}_i/\mathrm{PA}_{\mathrm{MeCP}}$ ratios give normalized contents of the A_i component in the feed mixture and in the product mixture. The definition of the reaction conversion C_i as the fraction of a compound consumed at time t is

$$C_i = (R_0 - R)/R_0. \tag{1}$$

The kinetic treatment of experimental data was discussed in detail in the previous article [8]. Briefly, the reaction scheme includes the following steps:

Equilibrium adsorption of an alkane molecule A on the active center C* (a highly acidic site on the catalyst surface capable of converting alkanes into carbocations),

$$[\mathrm{C}^*] + [\mathrm{A}_{\mathrm{gas}}] \overset{K}{\rightleftharpoons} [\mathrm{C}^* \ldots \mathrm{A}_{\mathrm{ads}}]. \tag{2}$$

An irreversible alkane ionization followed by a rapid skeletal isomerization of the parent carbocation,

$$[\mathrm{C}^* \ldots \mathrm{A}_{\mathrm{ads}}] \xrightarrow{k_1} [\mathrm{C}^{*-} \ldots \text{iso-}\mathrm{A}^+_{\mathrm{ads}}]. \tag{3}$$

Cracking of carbocations

$$[\mathrm{C}^{*-} \ldots \text{iso-}\mathrm{A}^+_{\mathrm{ads}}] \xrightarrow{k_2} [\mathrm{C}^* \ldots \mathrm{products}_{\mathrm{ads}}]. \tag{4}$$

Reversible desorption of the cracked products,

$$[\mathrm{C}^* \ldots \mathrm{products}_{\mathrm{ads}}] \rightleftharpoons [\mathrm{C}^*] + [\mathrm{products}_{\mathrm{gas}}]. \tag{5}$$

The assumption has been made [8] that the equilibrium in reaction (2) is established very rapidly. Application of the steady-state condition and the assumption that $[\mathrm{C}^*] > [\mathrm{A}_{\mathrm{gas}}]$ (see experimental section) gives

$$[\mathrm{C}^* \ldots \mathrm{A}_{\mathrm{ads}}] \approx K[\mathrm{C}^*][\mathrm{A}_{\mathrm{gas}}]. \tag{6}$$

Reaction (3) is the only step responsible for the disappearance of the initial alkane from the gas phase,

$$-\mathrm{d}[\mathrm{A}_{\mathrm{gas}}]/\mathrm{d}t = k_1[\mathrm{C}^* \ldots \mathrm{A}_{\mathrm{ads}}]. \tag{7}$$

Substitution of eq. (6) in eq. (7), integration of eq. (7) from $t = 0$ to t and combining the results with eq. (1) gives the following final relationship for reaction conversion C_i:

$$\ln[1/(1 - C_i)] = \ln(R_0/R) = k_1 K[\mathrm{C}^*]t. \tag{8}$$

This approach defines the reactivity of a particular alkane in the catalytic cracking reaction as a function of two parameters, the equilibrium alkane adsorption constant, K, and the carbocation formation rate constant, k_1.

4. Results and discussion

Fig. 1 shows the $k_1K[C^*]t$ values for a series on linear C_7–C_{20} alkanes at 250°C (at the total conversion of 2.6%) and in two experiments at 350°C (conversions of 18.1 and 7.3%, respectively). Because all components in the mixture are cracked together, the $[C^*]$ and t values for them are the same. The data confirm the well known effect: a rapid increase in *n*-alkane reactivity with the increase in their carbon number. These results are in a qualitative agreement with the previously published data on the cracking of individual *n*-alkanes [4–8]. *n*-alkanes predominantly form secondary carbocations in reaction (3),

$$CH_3{-}(CH_2)_x{-}CH^+{-}(CH_2)_y{-}CH_3.$$

It is reasonable to assume that the average energy requirements for the CH_2 group ionization in *n*-alkanes of various lengths (represented by k_1 values in eq. (8)) are similar. In such a case, the large differences in *n*-alkane reactivities in fig. 1 can be

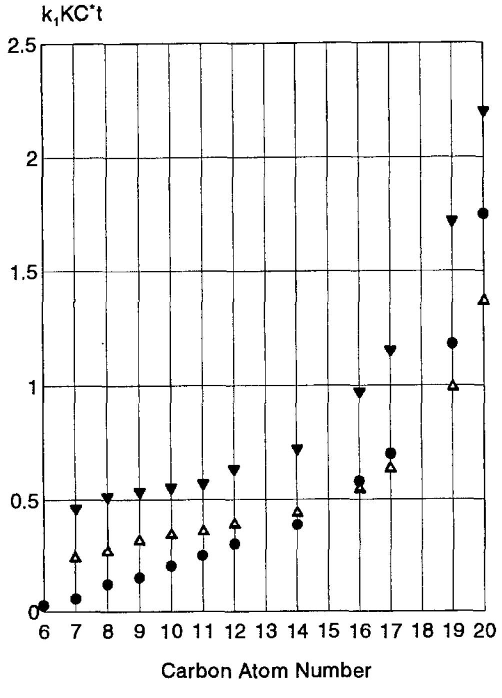

Fig. 1. Reactivities of linear alkanes in catalytic cracking over FSS-1 catalyst: (●) at 250°C, (▼) and (△) at 350°C (two consecutive experiments).

attributed to the differences in their equilibrium adsorption constants K. The increase in reactivity with the carbon number at 250°C is more pronounced than that in both experiments at 350°C. Two sets of measurements at 350°C in fig. 1 are virtually identical in shape. The differences between respective $k_1K[C^*]t$ values in these two experiments reflect a decrease in the active center concentration, $[C^*]$.

Fig. 2 compares the $k_1K[C^*]t$ values for linear alkanes and 2-methyl-branched alkanes at 350°C. As expected, reactivities of isoalkanes with one tertiary C–H bond are higher than those for *n*-alkanes, and these differences in reactivities increase with the carbon number. However, the differences between reactivities of linear and 2-methyl-branched alkanes are quite negligible for low molecular weight feeds.

Fig. 3 compares estimations of alkane reactivities in two types of experiments, cracking of individual alkanes (taken from ref. [8]) and cracking of alkane mixtures. The ordinate gives relative reactivities of alkanes normalized to the reactivity of 2-methylnonane. All experiments were carried out with the same catalyst at 350°C.

Several differences between the experimental results are apparent:

(1) The slopes of both curves for single-feed experiments (curves 3 and 4) are much steeper than for those describing multi-component experiments (curves 1 and 2).

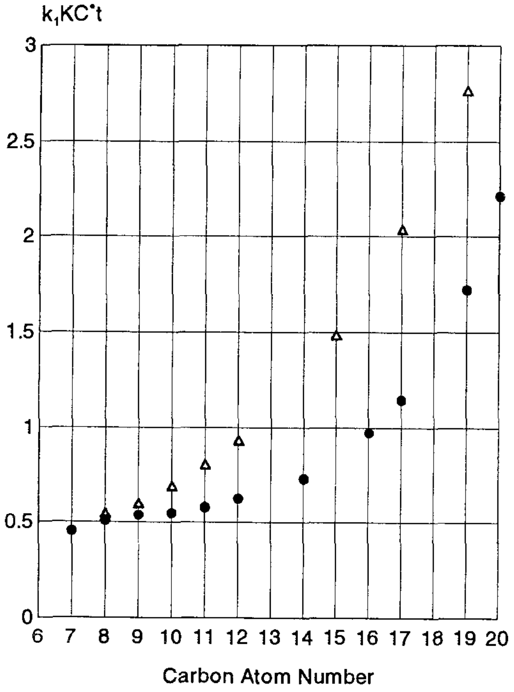

Fig. 2. Reactivities of linear (●) and 2-methyl-branched alkanes (△) at 350°C.

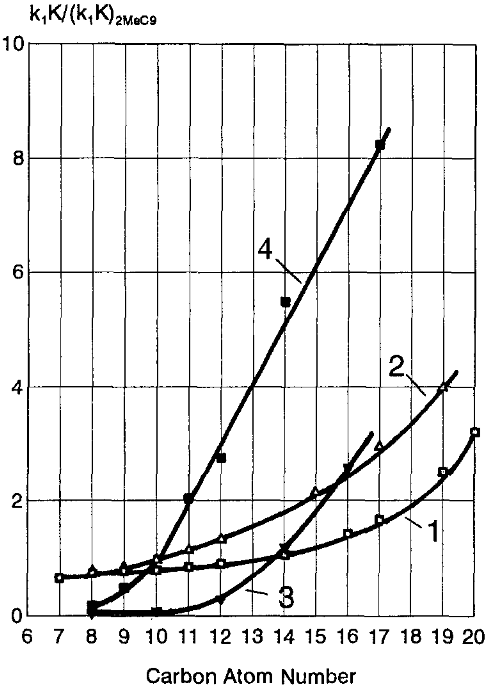

Fig. 3. Relative reactivities of various alkanes (normalized to reactivity of 2-methylnonane) at 350°C in multi-component experiments (linear alkanes – curve 1; 2-methyl-branched alkanes – curve 2) and in single-component experiments [8] (linear alkanes – curve 3; 2-methyl-branched alkanes – curve 4).

(2) The differences between reactivities of 2-methyl-branched and linear alkanes are much more pronounced in single-component experiments.

(3) Reactivities of all light alkanes in multi-component experiments (left parts of curves 1 and 2) are much higher than those in single-component experiments.

Because of the normalization, none of the differences can be attributed to the variations in the active site concentration, [C*], or the contact time *t*. A plausible explanation of the differences can be given if one regards two different pathways of carbocation formation from a particular alkane molecule. The first pathway involves an interaction between an adsorbed alkane molecule and an acidic center on the catalyst surface (reaction (3)). The second pathway involves hydride transfer between an alkane molecule and a carbocation [9–11],

$$R^+ + C_iH_{2i+2} \rightarrow R-H + C_iH_{2i+1}^+. \qquad (9)$$

Both the original carbocations formed in reaction (3) and light carbocations formed in the C–C bond fission (reaction (4)) are the probable participants in this reaction. The experimental data in fig. 3 can be rationalized if one assumes that the formation of the original carbocation in reaction (3) is a much more energetically demanding process than reaction (9), and that reaction (9) does not require preliminary adsorption of an alkane. In such a case, the presence of heavy components in hydrocarbon mixtures facilitates carbocation formation of lighter alkanes and thus make them more reactive. The data in fig. 3 imply that the reaction kinetics and relative alkane reactivities can differ very significantly between model experiments with individual alkanes and in the cracking of hydrocarbon mixtures.

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