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NOTES

Transformation of Hydrocarbons on Zeolites of Type Y

I. Promoting Effect of Olefins on the Rate of Catalytic Cracking of Paraffins

In 1949 Thomas (*1*) and Greensfelder *et al.* (*2*) postulated that olefin molecules could promote cracking reactions on amorphous alumosilicates. Later this proposal was confirmed for reactions of cetane cracking (*3, 4*) and isomerization of paraffins (*5, 6*).

The influence of unsaturated hydrocarbons on the rate of paraffins cracking was found (*7–11*) using the method based on the intermediate removal of olefins from the circulating reaction mixtures. By means of intermediate hydrogenation of unsaturated products resulting from *n*-octane cracking we have shown that the rate of paraffin cracking on the acid forms of Y zeolites and at low olefin concentrations is less than at higher olefin concentrations (*12, 13*). In the latter case the cracking reactions appear to be promoted by unsaturated products of cracking. We have studied the influence of olefin concentration in reaction mixtures on the rate and selectivity of *n*-octane splitting on Y zeolites containing various cations.

Decationation was performed by treating an initial form of NaY zeolite with 0.1 *N* solution of $NH_4Cl + NH_4OH$ and by periodic calcinating (between treatments) at 400–450°C for 3–4 hr (Kërrs method). Polyvalent cations were introduced in zeolites by (i) ion exchange between NH_4NaY zeolite and chloride solutions at pH 3–5 for La^{3+}, Y^{3+}, and Sc^{3+} cations; for readily hydrolyzing ions of Ti^{3+}, Hf^{4+}, and Al^{3+}, by (ii) sublimation of their chlorides on HNaY in a dry inert atmosphere.

All the experiments were carried out under concentration and temperature gradientless conditions in reactors with a fluidized catalyst bed or in a flow-circulation system.

A flow-circulation system with a reactor for the intermediate hydrogenation (*12*) was used to study the activity and selectivity of zeolites at olefin concentrations in the reaction mixture no higher than 10^{-3} mmole/liter. At the outlet of the reactor olefin concentration varied from 10^{-5} to 10^{-3} mmole/liter as a function of the mass of the catalyst.

An installation with a catalyst vibrofluidized bed (both pulse and flow versions) was employed to measure the activity and selectivity of zeolites in *n*-octane cracking at high concentrations of olefins, that is, under conditions of a fast deactivation of catalysts. Pseudo-steady-state conditions were ensured by using a mixture with a low concentration of paraffins and a pulse character of the activity measurements.

The catalytic activity of zeolites was determined as a ratio of the rate of *n*-octane cracking to octane concentration at the reactor outlet (W/C_8). The activities of zeolites in the hydrogen redistribution reactions were evaluated from the relative yields of paraffin and olefin hydrocarbons, C_2–C_5 (paraf/olef). The activity of zeolites in isomerization was determined from the ratio of isomers and paraffins C_4–C_5 of the normal structure (iso/norm).

A novel parameter has been introduced which we called a normalized residence time. It is calculated via formula (1) and is independent of the concentration of reactants in the reaction medium.

$$\tau = \frac{m}{C_{\text{in}} \cdot V_0 \cdot \Delta \cdot V} \tag{1}$$

where m is the mass of the catalyst in g; Δ is its bulk weight in g/ml; C_{inlet} is an octane concentration at the inlet in mmole/liter; V_0 is a mole volume of octane vapor at standard conditions; V is a volume of an intro-

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TABLE I

Composition and Properties of Zeolite Samples

Number	Sample	Na (%)	Content, % wt element	Atomic ratio Si/Al	Total content of cations in mg-equiv/g	Degree of crystallinity (%)
1	HNaY-I	2.2	—	2.0	1.0	100
2	HNaY-2	1.7	—	2.0	0.7	100
3	HNaY-3	1.4	—	2.0	0.6	90
4	HNaY-4	0.9	—	2.5	0.4	70
5	HNaY-5	0.6	—	2.5	0.3	80
6	HNaY-6	0.5	—	2.5	0.2	80
7	LaHNaY	1.0	3.7	2.5	1.2	50
8	YHNaY	0.8	2.1	—	1.0	70
9	ScNHaY	0.7	1.5	2.5	1.3	70
10	TiHNaY	0.9	0.9	2.5	1.0	—
11	HfHNaY	0.9	0.9	2.5	0.7	60
12	AlHNaY	1.0	1.6	2.5	2.2	60

duced mixture of reactants with an inert gas in liters/hr.

To eliminate diffusion limitations the grain fraction of 0.25–0.50 mm was used. Concentrations of reactants and reaction products were analyzed chromatographically on a column of 2.3 m in length filled with AW Hesasorb with polyphenyl ester at 120°C (octane) and on a column of 3.2 m in length filled with TZK with white paraffin oil at 65°C.

Crystallinity of zeolite framework was examined by X-ray analysis and by argon desorption. Prior to determination of the specific surface area, zeolite samples were dehydrated at 450°C for 3 hr. X-Ray patterns of zeolites were recorded on a URS-50 diffractometer on the Cu radiation for angles from 30 to 39°. The initial zeolite, NaY, served as an external reference.

Composition and physicochemical properties of zeolite samples investigated are compiled in Table I.

Figures 1a and b show the activity and selectivity as a function of the residence time for decationized zeolites, HNaY and ScHNaY, at olefin concentrations in the reaction mixture no higher than 10^{-3} mmole/liter. The change of the residence time by two orders of magnitude does not affect the W/C_8 value and selectivity of the process for both HNaY and ScHNaY. The rate of *n*-octane cracking in this region is described by the first-order equation with respect to the initial hydrocarbon concentrations. Variation of olefin concentrations from 10^{-3} to 10^{-5} mmole/liter does not change the reaction rate. A stable work of

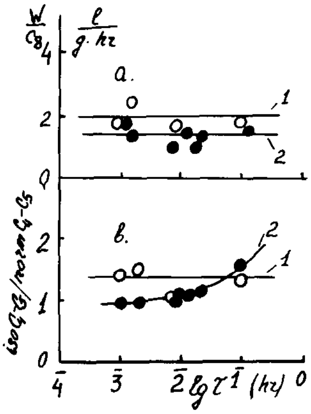

FIG. 1. Plot of W/C_8 (a) and iso/norm ratio (b) in products of *n*-octane cracking vs contact time for HNaY-4 zeolite (1) and ScHNaY (2) during experiments in a flow-circulation installation with intermediate hydrogenation. (Temperature of zeolite treatment, 550°C; AP-56 catalyst for hydrogenation, 350°C; reaction temperature of cracking and hydrogenation, 350 and 120°C, respectively; volume ratio *n*-octane : hydrogen = 1 : 100; P_H = 1.8 atm.)

the catalyst is observed under these conditions.

At olefin concentration in the reaction mixture higher than 10^{-3} mmole/liter zeolites undergo deactivation as a result of coke formation. After the first hour the activity of samples decreases by a factor of 3–5. In a pulse mode, catalysts do not undergo deactivation when passing 5–10 pulses of reactants. To calculate the initial activities of zeolites, the averaged data of the first three pulses were used.

The values of the initial catalytic activities and selectivities are given in Figs. 2a and b for a number of decationized sam-(olefin concentration 10^{-3}–10^{-1} mmole/liter) as a function of the normalized residence time.

The value of W/C_8 depends significantly on the residence time: for HNaY-I and HNaY-2 the activity is initially constant and then decreased by an order of magnitude. For highly decationized samples with a sodium content from 1.4 to 0.5%, extreme variations of the W/C_8 values with the residence time increase are observed. A fraction of C_4-hydrocarbon in the product of cracking is about 70–90%.

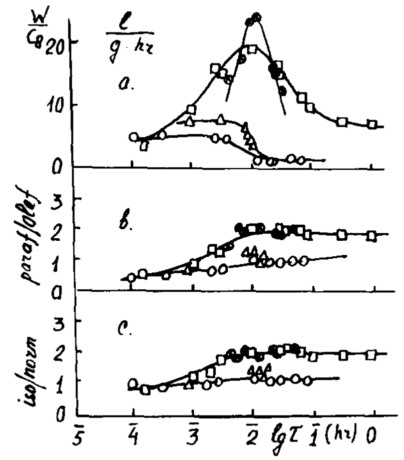

FIG. 2. Plot of W/C_8 (a), paraf/olef (b), and iso/norm (c) ratios in products of *n*-octane cracking vs contact time for decationized zeolite samples: HNaY-I (○), HNaY-2 (△), HNaY-4 (□), and HNaY-6 (⊗) during experiments in a pulse installation. (Temperature of zeolite treatment and cracking reaction, 450°C; volume ratio *n*-octane : helium = 1 : 100.)

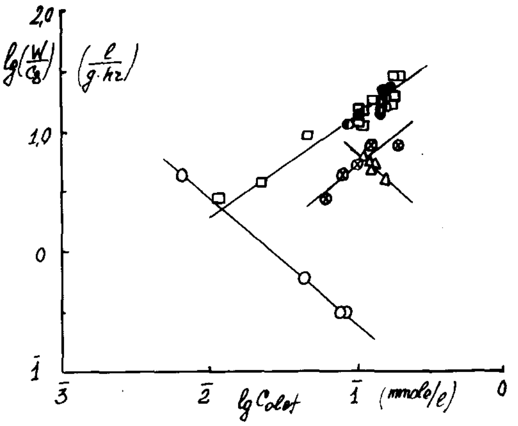

FIG. 3. Plot of W/C_8 vs concentration of olefin products of *n*-octane cracking for decationized zeolite samples: HNaY-I (○), HNaY-2 (△), HNaY-3 (⊗), HNaY-4 (□), HNaY-5 (●), and HNaY-6 (◐).

At a small catalyst weight the residence time is less than 10^{-3} hr (the conversion degree is 1–2%), the catalytic activity is low, and the paraf/olef and iso/norm ratios observed are equal for different samples. At a high value of τ the W/C_8 as well as the paraf/olef and iso/norm ratios are changing extremely. For highly decationized samples the redistribution and isomerization activities grow more rapidly than for samples containing 2.2 and 1.7% wt Na. Note also that at $\tau \leq 10^{-3}$ the paraf/olef ratio is far less than unity.

Values of W/C_8 as a function of the concentration of olefin in the reaction medium are shown in Fig. 3. For zeolite samples containing 2.2 and 1.7% wt Na, the value of W/C_8 decreases as the concentration of unsaturated products is increased. In this case, the rate of cracking is described by the kinetic equation of the type

$$W = K_1 \cdot C_8H_{18} \cdot C_{\text{olef}}^{-1}. \qquad (2)$$

For samples containing 1.4–0.5% wt Na, W/C_8 increases as C_{olef} is increased. The reaction order with respect to olefin products observed in this case has a positive value close to unity. The kinetic equation is of the form:

$$W = K_2 \cdot C_8H_{18} \cdot C_{\text{olef}}. \qquad (3)$$

The data obtained on the catalytic activity and selectivity for a number of zeolites with polyvalent cations are presented in Figs. 4a, b, and c. The main product of cracking is C_4-hydrocarbon (70–90%). It is seen that at small residence times the catalytic activity is low and the paraf/olef and iso/norm ratios are almost the same for different catalysts. An increase of the residence time leads to an increase of the activity, redistribution, and isomerization ability of the catalysts. An increase of the activity and of the paraf/olef and iso/norm ratios is greater for samples with higher *e/r* value. It should be noted that for the cation-containing zeolites the paraf/olef ratio becomes far less than unity as the residence time is decreased.

Figure 5 shows the plot of W/C_8 vs the concentration of unsaturated products for zeolites with polyvalent cations. For all the catalysts, W/C_8 increases as C_{olef} is increased. The reaction order with respect to olefin products is close to unity in agreement with Eq. (3). In all the cases the ratio $i\text{-}C_{4/\text{norm}}\text{-}C_4$ is in the range 1–2.0, i.e., is greater than it must be at thermodynamic equilibria for given conditions.

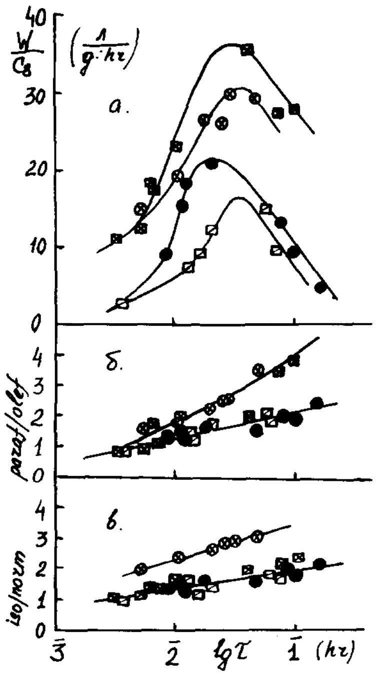

FIG. 4. Plot of W/C_8 (a), paraf/olef (b), and iso/norm (c) ratios in products of *n*-octane cracking vs contact time for zeolite samples with polyvalence cations: YHNaY (□), ScHNaY (●), TiHNaY (⊗), and HfHNaY (■). (Temperature of zeolite treatment and cracking reaction, 450°C; volume ratio *n*-octane : helium = 1 : 100.)

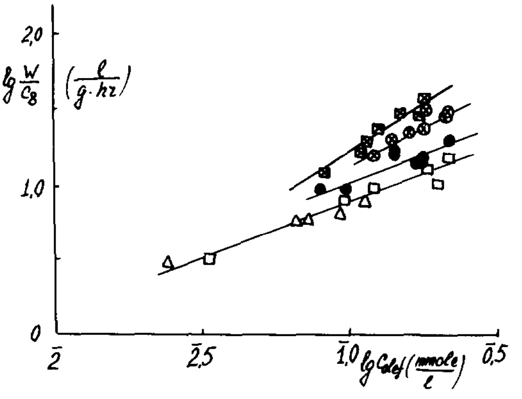

FIG. 5. Plot of W/C_8 versus concentration of olefin products of *n*-octane cracking for zeolites with polyvalence cations: LaHNaY (△), YHNaY (□), ScHNaY (●), TiHNaY (⊗), and HfHNaY (■).

The study of *n*-octane cracking at low concentrations of olefins in the reaction media on zeolites with various cations has shown that (i) all catalysts are not poisoned by coke, and (ii) for all the samples the rate of *n*-octane cracking follows the first-order equation with respect to the concentration of *n*-octane and is independent of the concentration of unsaturated products.

From the study of the process of cracking at high concentrations of olefins in reaction media the following conclusions may be drawn:

(1) all samples are subjected to deactivation by coke;

(2) for all catalysts other than HNaY-I and HNaY-2, the rate of cracking depends upon the residence time extremely;

(3) for all samples the rate of *n*-octane cracking depends upon the concentration of olefin products;

(4) at small residence time the selectivity is almost the same for all catalysts. Upon increasing τ, an increase of the paraf/olef and iso/norm ratios occurs.

Thus at small concentrations of olefins (small conversion degree) the reaction rate of *n*-octane cracking was shown to be independent of the concentration of olefin products. The shape of the kinetic equation suggests that splitting of molecules of the initial product proceeds without inclusion of olefin molecules into an active complex, that is, through the direct interaction of hydrocarbon with the catalyst active sites (e.g., by the hydride-ion transfer). Small paraf/olef ratios obtained by extrapolation to the region of low τ allow us to propose that olefins are the main products of the primary splitting. In general, the transformation at this step may follow the scheme:

$$C_8H_{18} + A^{*}\text{-Zeol.} \rightleftarrows 2\ C_4H_8 + H_2 + A^{*}\text{-Zeol.}$$

At low concentrations of olefin products secondary reactions, in particular reactions of coke formation and redistribution of hydrogen, do not occur. This idea is supported by the fact that zeolites are characterized by stable work during prolonged tests. Hence this type of transformation may be termed as the range of primary reactions.

It should be noted that in this region of olefin concentrations the selectivity with respect to isomer yields remains constant for different catalysts. This may be evidence for the common nature of active sites therein which catalyze the initial step of paraffin transformation. An increase of the decationation degree and variation of the nature of introduced polyvalent cations affect only the number of these sites.

At high concentrations of unsaturated products in a reaction flow the reaction rate depends on their concentration and, in this case, a process as a whole may be considered to be autocatalytic (*14*).

Olefins may be involved in the reaction by modifying active centers of the zeolite framework to give small carbonium ions via the mechanism proposed in Refs. (*1*, *2*) for amorphous alumosilicates and examined by Cant and Hall (*15*) for acid–base transformations on zeolites.

$$C_4H_8 + \text{HO-Zeol} \rightleftarrows C_4H_9^{+}O^{-}\text{-Zeol.}$$

$$C_8H_{18} + C_4H_9^{+}O^{-}\text{-Zeol.} \rightleftarrows C_4H_8 + C_4H_{10} + C_4H_9^{+}O^{-}\text{-Zeol.}$$

According to this mechanism, an increase of olefin concentration not only leads to the growth of the number of active sites (small carbonium ions) but also provides a new route, probably through the hydride-ion transfer from the molecule of the initial substance onto these new active groups. However, another action of olefins should be noted too: they inhibit the process of cracking due to simultaneously proceeding reactions of coke formation. The shape of the kinetic equation for HNaY-I and HNaY-2 catalysts indicates that for zeolites with Na content exceeding 1.4% *n*-octane cracking occurs with a predominant inhibition by the product. On the other catalysts the process is predominantly autocatalytic. In this case, the selectivity depends both on the catalyst composition and the conversion degree of the reactants. This range of cracking processes may be called as a range of secondary transformations.

Thus the process of cracking as a whole involves at least two steps: a primary reaction that in terms of autocatalysis may be called an inducing reaction and that leads to the formation of olefins which perform the function of cocatalysts at the second step. At the second step these products take part in the formation of new highly active sites and thus open a new reaction route.

As far as the first step is concerned, it is valid to propose that catalysis of paraffin cracking occurs on active surface sites unmodified by hydrocarbons. Olefins are the main products of this transformation step. The second step proceeds through the interaction of reactants with the surface carbon products which are olefin complexes with active surface sites.

High concentrations of olefins in the reaction medium lead to the acceleration of transformations of olefins themselves, specifically, reactions of hydrogen redistribution and alkylation accompanied by the formation of saturated isomerized and condensed products.

In the range of the secondary cracking the yield of isomerized C_4-products is higher than at thermodynamic equilibrium and in the range of primary cracking. This is possible if the cracking includes alkylation of carbonium-ion by olefins leading to the formation of a branched carbonium-ion and then to the elimination of isomerized saturated fragments.

The branched structures are decomposed at a significantly higher rate than weakly isomerized compounds. This also contributes to the increase of the overall rate of cracking. In this case primarily isomerized fragments are split, thus leading to a greater amount of isomers in products than might be expected for thermodynamic equilibrium conditions.

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