SOME PECULIARITIES OF HYDROCRACKING OF PARAFFINS ON METAL-ZEOLITE CATALYSTS

By

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In the light of recent data on zeolites as catalysts their capacity for polyfunctional catalytic action may be considered as the most important feature. This capacity is related to the presence in zeolites of the catalytically active sites of different nature. The question arises: are general ideas of bifunctional transformations of paraffins on metal-nonzeolite catalysts, considered by WEISZ [1] and THOMAS [2], valid for zeolite systems as well?

One of these regularities — the dependence of the catalyst activity on the activity ratio of acidic and metallic components was confirmed for zeolite catalysts: the rate of hydrocracking was shown to increase significantly with the acidity of a support in the series Pd/REZ<Pd/HY [3] or Al_2O_2<HY<H-mordenite [4]. As the hydrogenating activity of catalysts falls, the total rate [5] and the yield of isomerized hydrocarbons [6] also decrease.

However, simple schemes of bifunctional transformations listed in [1] may be significantly complicated by a number of factors: 1) olefins, being intermediates of transformations, may promote reactions of cracking and isomerization [7]; 2) metal dispersion in zeolites may result in appreciable changes of their specific catalytic activity toward hydro-dehydrogenation; 3) when metallic component is fixed inside zeolite cavities, diffusional effects may influence the total rate and selectivity of hydrocracking. Taking this into account, the following problems were mainly studied at the Institute of Catalysis: the influence of olefin concentration on the activity of acidic component of hydrocracking catalysts; the influence of the metal component dispersion on its specific activity in hydrogenation of olefins; the influence of the activity ratio of acidic and metallic components and the homogeneity of their mutual distribution on the activity and selectivity of hydrocracking of paraffins. N-octane, octene-1, hexene-1 were chosen as model hydrocarbons.

Experimental

A flow-circulation installation supplied with a cracking reactor working at 350 °C and a hydrogenating one working at 150 °C as well as a pulse installation with a catalyst fluidized bed were employed to study the role of olefins during transformation of hydrocarbons on the acidic component of the hydrocracking catalyst (HY

zeolite). This system allowed changing the olefin concentration in the reaction medium over the 10^{-1}—10^{-6} mmol/1 range.

The specific hydrogenating activity of the metallic component in metal-zeolite catalysts was determined by the relation between the rate of hexene-1 hydrogenation measured in the flow-circulation installation at 150 °C and the metal surface area found from the oxygen chemisorption value.

The rate and the selectivity of hydrocracking was measured in the flow-circulation installation (300 and 350 °C, pressure 1.8—20 atm, $H_2:C_8H_{18}=100$). The metal dispersion in zeolites was varied according to the procedures described in [8].

Results and discussion

The decrease in the olefin concentration in the reaction mixture from 10^{-1} down to 10^{-3} mmol/1 (Fig. 1) resulted in a sharp (by a factor of 30) fall of the rate of n-octane cracking. Moreover, the isomerized to normal reaction products ratio was also decreased by a factor of 2. At low olefin concentrations the catalyst activity is unchanged with time; the process of cracking may be described by the kinetic
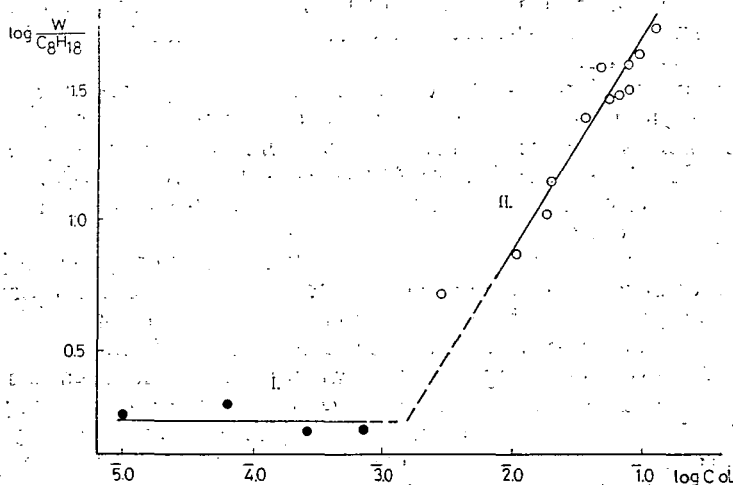

Fig. 1. Influence of the concentration of C_3—C_5 olefins in the reaction mixture on the rate of n-octane cracking, reaction temperature 350 °C

equation of the first order with respect to n-octane, $W=K_1C_8$. At high olefin concentrations the rate of cracking depends on the amount of olefins in the reaction mixture, the kinetic dependence is of the $W=K_2C_8C_{olef}$. type. The catalyst activity falls quickly with time.

The rate of octene-1 cracking under standard conditions of cracking is much higher than that of n-octane and the rate ratio octene-1:octene is 50:1. As it can be seen from Fig. 2, with the increase of nickel and palladium dispersion in HY zeolite (0.9% wt Na) the metal specific activity toward hydrogenation of hexene-1 changes
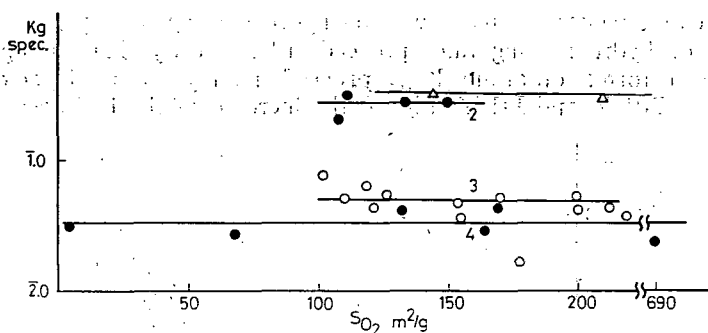
Fig. 2. Rate constant of hexene-1 hydrogenation as a function of the surface area of the metallic component, reaction temperature 150 °C, 1 — zeolite PdHY, 2 — Pd/Al_2O_3, 3 — zeolite NiHY, 4 — Ni/SiO_2
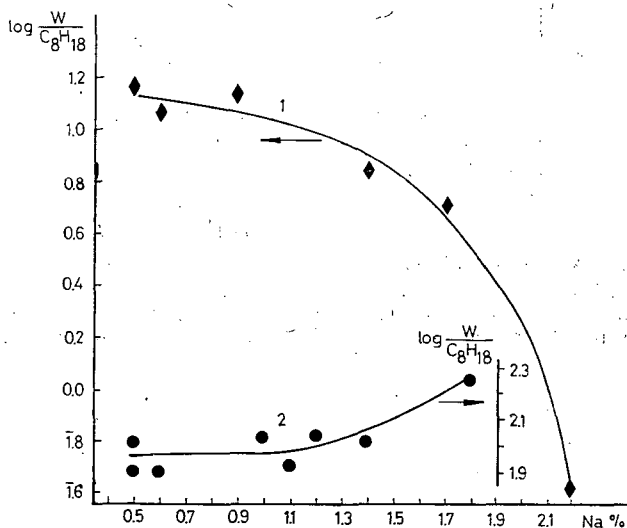

Fig. 3. Influence of sodium concentration in zeolite component on the rate of *n*-octane cracking. Reaction temperature 350 °C, pressure 1.8 atm.; 1 — cracking of *n*-octane on HY, 2 — hydrocracking of *n*-octane on NiHY

slightly and is almost similar to that of these metals in the catalysts considered. The character of variations in the activity of acidic components HY and NiHY depending on sodium concentration has been compared (Fig. 3). The activity of the former one continuously increases with the fall of sodium concentration, for the latter one variations in sodium concentration from 0.5 to 1.2% wt practically do not affect the activity and selectivity. Fig. 4 gives the dependence of the rate of *n*-octane hydrocracking on the activity of the metallic component. The rate of *n*-octane transforma-

tion toward all directions increases with the hydrogenating activity. At $\log K_{hydr.} < 2.8$ increasing of hydrocracking rates proceeds more slowly than at $\log K_{hydr.} > 2.8$. N-octane transformation at any $K_{hydr.}$ proceeds mainly toward the acidic cracking. For zeolites PdHY and PtHY (Fig. 5) the increase of the hydrogenating activity
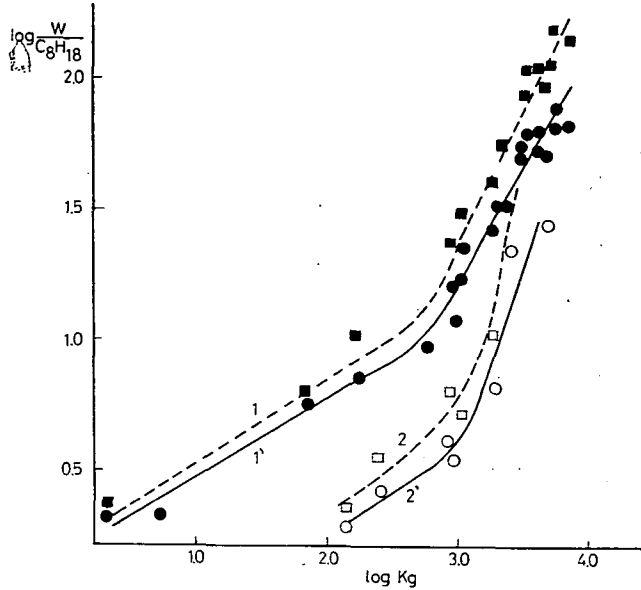

Fig. 4. Influence of the activity of nickel component on the rate of hydrocracking (1,2) and on the rate of product formation of n-octane acidic splitting (1′, 2′), reaction temperature 350 °C, pressure 1.8 atm; 1,1′ — zeolite NiHY, 2,2′ — mechanic mixture NiO+HY
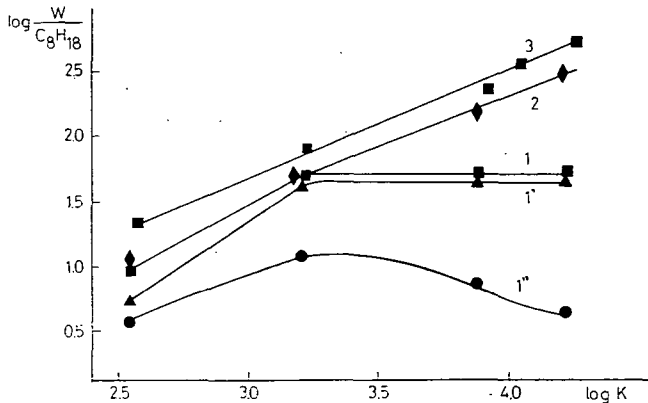

Fig. 5. Influence of the activity of the metallic component in PtHY on the overall rate of hydrocracking of n-octane (1) and isooctane (3) in hydrogen and of n-octane in helium (2). The yield of products of isomerization (1′) and n-octane cracking (1″) in hydrogen·

results in the decrease of the selectivity toward the acidic cracking and in the increase of the rate of octane isomers formation. For catalysts with high hydrogenating activities the predominant direction of transformation is hydroisomerization (70—80%). When hydrogen is replaced by helium on zeolites PtHY the formation rate of the acidic cracking products drastically increases, while the rate of hydroisomerization falls. Hydrocracking of *iso*octane on zeolites PtHY is characterised by significantly higher rate than that of hydrocracking of *n*-octane and by the predominant direction toward splitting reactions.

In the case of mechanic mixtures (Fig. 4) at low activities of the metallic component the transformation is primarily directed toward reaction of the acidic cracking (80—90%) while on catalysts with high hydrogenating activities — toward hydrogenolysis reactions (60—70%). In addition, over the whole range of $K_{hydr.}$ values the overall rate of hydrocracking, the yield of isomerized products of acidic splitting and isomerization are considerably less than those in the case of homogenized zeolites.

The experimental results (cracking of *n*-octane on zeolite HY, Fig. 1) permit us to determine the region wherein the rate of cracking is independent of olefin concentration. Apparently, at low olefin concentrations the activation of molecules of initial paraffin is due to their direct interaction with the surface active sites, probably, through separation of hydride-ion and formation of carbonium-ion according to the scheme described in [9]:

$$C_8H_{18} \xrightarrow{-H^-} C_8^+H_{17} \rightarrow i - C_8^+H_{17} \xrightarrow{\text{cracking}} \quad (I)$$
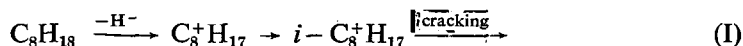
The rate of acidic splitting, in this case, is rather slow and iso:normal products ratio is close to unity (1.3—1.4).

When the rate of cracking depends on olefin concentrations it may be proposed that olefin must be involved in the intermedate complex, *e.g.* according to the following scheme:
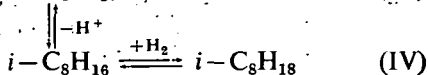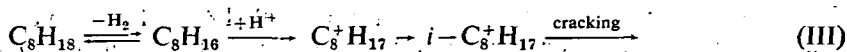
$$C_4H_8 \xrightarrow{+H^+} C_4H_9^+ \xrightarrow{+C_8H_{18}} i - C_{12}^+H_2 \xrightarrow{\text{cracking}} \quad (II)$$
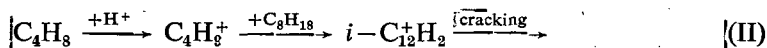
Cracking proceeds at a high rate giving large amounts of isomerized products (iso/n = =3—4). However, intensive processes of coke formation are also observed.

Likewise in the case of cracking, under hdyrocracking conditions the mechanism and the rate of stages of acidic transformation of hydrocarbons on zeolite component should depend on olefin concentration in the reaction zone. The latter must depend on the activity of the metallic component in the metal-zeolite catalyst. With increasing the activity of the hydrogenating component and, hence, decreasing the concentration of short olefins in the reaction zone, gradual transition from paraffin transformation *via* scheme II to scheme I might be expected. In this case, on the one hand the processes of coke formation will be slowed down, on the other hand, the rate of cracking promoted by olefins should decrease. Actually observed slight increase in the rate of hydrocracking on nickel-zeolite catalysts with their hydrogenating activity in the first region (Fig. 4) may be explained by the decrease in the extent of coke formation on acid sites.

One might expect that further increase of the hdyrogenating activity, decreasing the olefin concentration in the reaction zone, should lead to the fall of the rate of hydrocracking. From this point of view, sharp development of cracking (Fig. 4) on catalysts with high hydrogenating activities (log K > 2.8) is unexpected and may

be explained only by transition to another mechanism: from the initial stage of dehydrogenation of n-octane to more reactive octenes:

$$C_8H_{18} \underset{-H_2}{\rightleftharpoons} C_8H_{16} \xrightarrow{+H^+} C_8^+H_{17} \rightarrow i-C_8^+H_{17} \xrightarrow{cracking} \quad \text{(III)}$$

$$\Big\| {-H^+}$$

$$i-C_8H_{16} \underset{+H_2}{\rightleftharpoons} i-C_8H_{18} \quad \text{(IV)}$$

In fact, the increase in the activity of the metallic component is accompanied by a double effect: i) the concentration of short olefin products of cracking is decreased due to the growth of the hydrogenation reaction rate, ii) the formation rate of octenes — products of dehydrogenation — is increased. Though in the thermodynamic sense the formation of octenes is less probable, the presence of a splitting component results in their quick acidic transformation into the thermodynamically-probable products as well as in the increase of the overall rate of paraffin transformation.

One of the peculiarities of zeolite catalysts is the fact that owing to a high activity of the acidic component, the reaction stage proceeding on a metal is rate-determining. Only by decreasing the reaction temperature down to 300 °C and by addition of Pt as a hydro-dehydrogenating component such ratio of activities of acid and hydrogenating components was reached at which the stage of acid-base transformations became rate-determining (Fig. 5). In this case the rate of splitting falls and n-octane transformation proceeds primarily toward hydroisomerization. It is likely that, in this case, splitting of the $C-C$ bond in the intermediate (path III) becomes less probable than proton elimination (path IV). The substitution of hydrogen by helium, leading to the termination of hydrogenation (Fig. 5, curve 2), must cause drastic increase in olefin concentration in the reaction zone. In this case, transformation via path III becomes predominant.

The results obtained could be explained assuming that the stages of formation and isomerization of carbonium-ion are reversible (scheme IV). Although the formation of products of cracking is thermodynamically more probable than proton elimination, when increasing the hydrogenating activity the kinetic factor rather than the thermodynamic one may become determining.

If this assumption could be valid, introduction of the hydrogenating reactor in transformation via scheme I should be accompanied by the increased yield of isomerized octanes. However, this fact has not been actually observed. Moreover, during hydrocracking of isooctane in the presence of PtHY catalysts the main reaction direction was acidic cracking (Fig. 5). Hence, a more valid proposal may be made which enables the explanation of all above facts, $i.e.$ $C-C$ bond breaking must be preceded by the formation of a strongly-isomerized carbonium-ion.

Formation of multi-branched structures may take place after the secondary interaction of short olefins from the gas phase with a carbonium-ion on the catalyst surface. If the activity of a hydrogenating agent is negligible (or it is not used) (paths III and II) the concentration of olefins in the reaction zone is sufficient to carry out reactions of alkylation accompanied by breaking of the $C-C$ bond of the multi-branched structure formed.

Introduction of either a hydrogenation reactor (scheme I) or a strongly-hydrogenating component (PtHY) into the catalyst results in a drastic fall of short olefin concentration. Due to this the possibility for the formation of multi-branched

structures through alkylation of carbonium-ion with olefin is lowered and reactions of C—C splitting are inhibited.

Thus, the change in the ratio of activities of acidic and hydrogenating components in the metal-zeolite catalyst must lead *i*) to the change in the path of paraffin transformation and *ii*) to the change in the rates and the mechanism of the stages of transformation on the catalyst acidic component.

Owing to the fine-pore structure of zeolites and their high activity, the processes of diffusional transfer between various sites may play a significant part in metal-zeolite catalysts.

Thus the increase of the homogeneity of the metal-zeolite system (by addition of a metal inside zeolite cavities) must provide higher (than in the case of mechanic mixtures) rates of paraffin transformation due to weakening of diffusional effects inside zeolite cavities.

References

[1] *Weisz, P.:* Adv. in Catal. **13**, 137 (1962).
[2] *Thomas, J., Y. Thomas:* Heterogeneous Catalysis, "Mir", M., 1969.
[3] *Voorhies, A., W. Hateher:* JEC Product Research Develop. **11**, 46 (1972).
[4] *Jan, T. J.:* J. Catal. **25**, 204 (1972).
[5] *Swift, H. E., E. C. Breck:* JEC Product Research Develop. **13**, 106 (1974).
[6] *Schulz, H., J. Weitkomp:* JEC Product Research Develop. **11**, 46 (1972).
[7] *Andrianova, T. A., S. Z. Roginskii:* Problemy Kinetiki i Kataliza, Izd. AN SSSR, Moscow, v. IX, 1957.
[8] *Ione, K. G., P. N. Kuznetsov, V. N. Romannikov, N. V. Klueva:* Primenenie Zeolitov v Katalize, Izd. Nauka, 1977, p. 81.
[9] *Leftin, H. P.:* Carbonium Ions, Ed. G. A. Olah, P. V. R. Schleyer, v. **1**, 1972.