JOURNAL OF CATALYSIS 10, 166–174 (1968)

Zeolitic Aluminosilicate

I. Surface Ionic Diffusion, Dynamic Field, and Catalytic Activity with Hexane on CaY

SHAO E TUNG AND EDWARD McININCH

From the Central Research Division Continental Oil Company, Ponca City, Okalahoma

Received October 9, 1967; Revised December 5, 1967

Hexane cracking and isomerization of CaY catalysts were studied. A new type of activity was found to set in at the 60% level of exchange (Ca^{2+} for Na^+). The attributes unique to these high Ca^{2+} (>60%) catalysts are pointed out. The appearance of these attributes coincided surprisingly closely with the inauguration of the surface electric field from the electrostatic and crystallographic considerations.

A concept of *dynamic* (*time-variant*) *surface field* is introduced, and the dynamic situation is assumed to arise from the surface diffusion of cations. These dynamic characteristics render the sites capable of activated adsorption and subsequent desorption and thereby continuously promote catalytic reactions in a cyclic manner. A reaction mechanism is proposed. The operation of the proposed mechanism relies upon the *dynamic* nature of the surface field.

INTRODUCTION

While the significance of the Brönsted acids in promoting a number of surface reactions (e.g., alkylation, dealkylation, and olefin polymerization) on a zeolite surface can hardly be disputed, some reactions remain for which reaction sites other than Brönsted acids seem to be involved. Notable among such reactions are alkane isomerization and cracking. It is known that silica-alumina does not or virtually does not activate carbon–hydrogen bonds. If one attributes this catalytic activity toward alkanes of zeolites to Brönsted acids, then one would have to assume that the Brönsted acids on zeolites behave in a drastically different way from the Brönsted acids on silica-alumina. Otherwise, one may attribute this activity to the surface sites not readily available on the silica-alumina surfaces. For the purpose of elucidation, hexane cracking and isomerization reactions over CaY catalysts with the varying levels of Ca^{2+} content were studied in detail. It is hoped that the results may help define the unique attributes of the reactions of hexane on CaY surfaces. From these attributes, we hope that the reaction mechanism may be deduced and that the nature of catalytic sites may be explored.

EXPERIMENTAL PROCEDURE

The NaY was supplied by the Linde Company. The Ca^{2+} for Na^+ exchange was conducted according to the conventional procedure using Fischer Scientific $CaCl_2$ (anhydrous, 99.9% assay). The Na^+ in all the samples was analyzed by flame photometer and the Ca^{2+} by X-ray fluorescence. The level of exchange, defined as the percent of the original Na^+ replaced, was determined to be 90%, 83%, 75%, 70%, 66%, 49%, 33%, and 19%.

The microreactor used for these reactions is similar to the one reported on previously (*1*). All catalyst preparations were precalcined in air by heating in a crucible to 230°C over a period of 3 hr and were held at that temperature for 3 hr. A total of 0.9 g of the precalcined catalyst in the form of a fine powder was weighed into the reactor tube and was further calcined in situ at 550°C. This involved heating to 550°C over a period of 3 hr and holding at that temperature for 2 hr. During the calcination, air was allowed to flow through the catalyst at a rate of 25 ml/min. After the calcination, the catalyst was purged with nitrogen at the same rate for about an hour before tht catalyst as cooled down to the reaction temperature.

When the catalyst was properly cooled down to the lowest temperature level covered in the study (300°C), the nitrogen flow was discontinued and *n*-hexane (Phillips pure grade 99.96 mole % purity) was fed in as a liquid at a fixed rate of 3 ml/hr, which with 0.9 g of catalyst (3-ml apparent volume) in the reactor gave a LHSV (liquid hourly space velocity) of 1.0. Both liquid product and gas product were collected and were measured.

A total of 2 ml of feed was passed through the reactor at one temperature level. The liquid product taken during the last ½-ml feed was analyzed, as were the gas samples which were taken at the end of the run for each temperature level. Six temperature levels were covered, ranging from 300° to 550°C at 50° increments.

The following analyses were made to secure a complete product distribution pattern:

(1) Gas analysis for hydrocarbon components using a 15-ft HMPA (hexamethyl phosphoramide) column and a hydrogen flame detector. This analysis gave a good separation of C_1 through C_5 with the exception of ethane and ethylene.

(2) Gas analysis with an 18-inch silica gel column in series with the HMPA column and a hydrogen flame detector for ethane and ethylene.

(3) Gas analysis with an 8-ft silica gel column and a thermal conductivity detector for hydrogen and methane.

(4) Liquid analysis for aliphatic hydrocarbon compounds from C_1 to C_6 using a

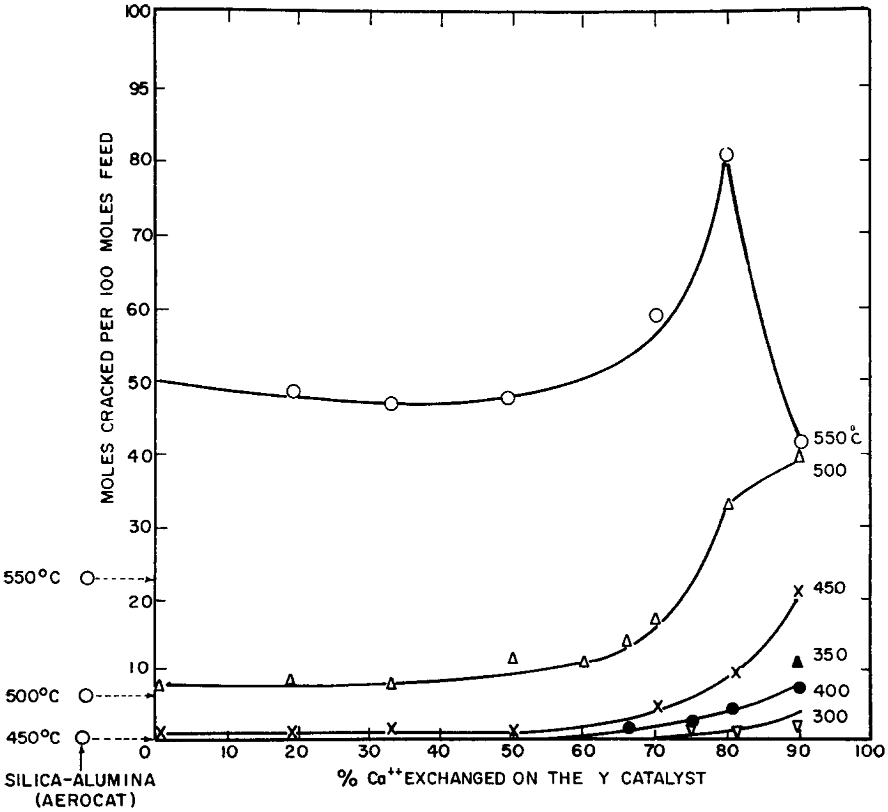


FIG. 1. Rate of cracking versus catalyst composition.

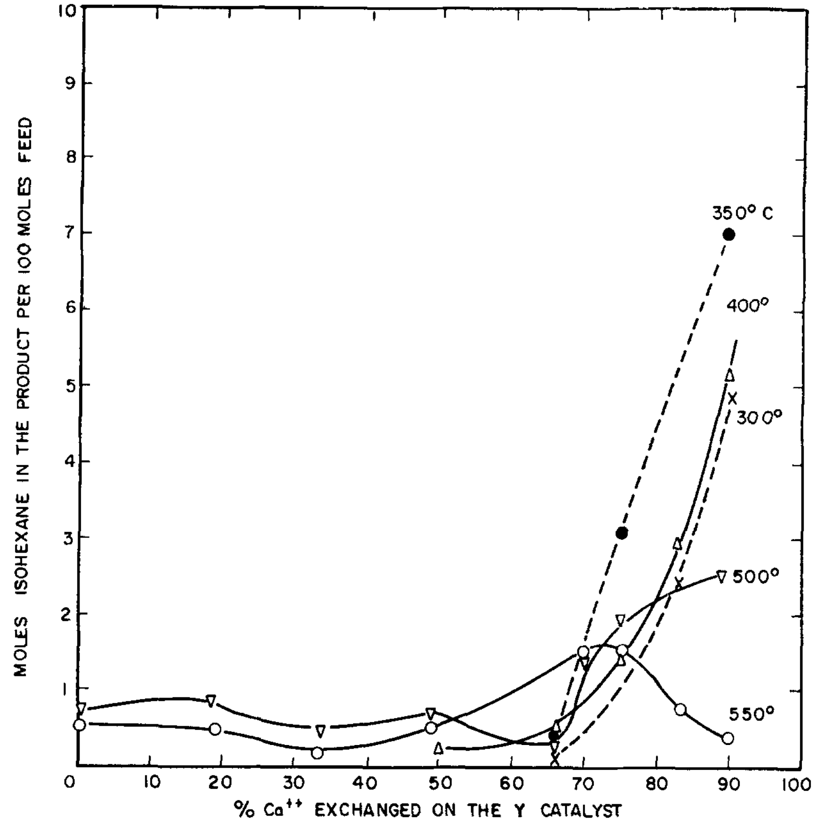


FIG. 2. Rate of isomerization versus catalyst composition.

15-ft, 30% α-methylnaphthalene column. The column was cooled to —30°C and was slowly raised to 30°C during the period of analysis, which was about 110 min.

(5) Liquid analysis by mass spectrometer for post-hexane components.

RESULTS

The variation of rates of cracking versus catalyst composition in terms of the level of exchange (Ca^{2+} for Na^{+}) is plotted in Fig. 1. For the purpose of comparison, the rate pertaining to the silica-alumina is indicated by an arrow on the left side of the figure. It shows that the Y-type zeolite, even in its sodium form, is more reactive than the silica-alumina catalyst for cracking. As more and more Na^{+} was replaced by Ca^{2+}, the cracking activity of the catalyst did not change materially until about 60% of the Na^{+} was replaced. Further increases of Ca^{2+} increased the cracking activity sharply.

Variation of the isomerization activity with the level of exchange exhibits a parallel characteristic with the cracking activity. Thus in Fig. 2, a turning point at around 60% is again observed, in agreement with observations previously made by Pickert *et al.* (*2*). While the cracking activity increased steadily with temperature, the isomerization increased at first, reached a maximum at 350°C, and then decreased. This can be attributed to the fact that isomerization and cracking are competitive reactions and that high temperature favors cracking. Silica-alumina behaved similarly to the Na form of the Y-type zeolite and had very little activity for alkane isomerization.

Some typical product distributions for Ca(83%)Y, Ca(70%)Y, Ca(19%)Y, Ca (0%)Y, and silica-alumina are summarized in Table 1. This table shows that the products generated by the high Ca^{2+} (i.e., >60% Ca^{2+}) catalysts differ significantly

TABLE 1
PRODUCT DISTRIBUTION OF *n*-HEXANE AT 450°C

	CaY-0%	CaY-19%	CaY-70%	CaY-83%	Silica-alumina[a]
Reaction products (mole %)					
Hydrogen	0.2	0.1	0.1	0.2	0.4
Hydrocarbons	99.8	99.9	99.9	99.8	99.6
	100.0	100.0	100.0	100.0	100.0
Hydrocarbon distribution (on H_2- and C_6-free basis)					
		Carbon Number			
C_1	18.9	13.7	3.9	4.2	6.9
C_2	30.0	23.7	6.1	6.9	6.8
C_3	30.3	37.4	50.8	41.6	49.1
C_4	13.9	11.4	23.3	25.3	25.4
C_5	6.9	11.9	8.9	16.3	9.7
		1.9	5.0	5.7	2.1
	100.0	100.0	100.0	100.0	100.0
		Components			
Methane	18.9	13.7	3.9	4.2	6.9
Ethane	30.0	11.4	4.8	6.0	6.8
Ethylene		12.3	1.3	2.9	
Propane	16.0	16.6	33.2	33.3	22.3
Propylene	14.3	20.8	17.6	8.3	26.8
Isobutane	4.5	0.5	11.9	15.5	6.3
n-Butane	3.3	1.9	7.8	7.8	5.9
Butenes	6.1	9.0	3.6	2.0	13.2
Isopentanes	3.0	0.5	4.9	12.2	2.8
n-Pentanes	1.2	6.2	2.3	2.6	1.1
Pentenes	2.7	5.2	1.7	1.5	5.8
Benzene	—	—	1.6	0.9	—
Xylene	—	1.9	1.4	—	—
Toluene	—	—	1.2	1.9	2.1
C_3-Substituted benzene	—	—	1.4	1.9	—
Naphthalene	—	—	1.4	1.0	—
	100.0	100.0	100.0	100.0	100.0

[a] Aerocat 2000, manufactured by American Cyanamide Company.

from those generated by low Ca^{2+} catalysts. Ca(83%)Y and Ca(70%)Y yield predominantly C_3 and C_4 with relatively small amounts of C_1 and C_2. This resembles the carbonium ion mode of cracking over silica-alumina. With Ca(19%)Y and Ca(0%)Y, more C_1 and C_2 were observed. At higher temperatures, the difference became less distinct, presumably because some C_3 and C_4 were further cracked over Ca(83%)Y and Ca(70%)Y catalysts.

While the cracking products from the high Ca(>60%)Y catalysts at 450°C resemble those over silica-alumina in terms of carbon number distribution, they differ from the latter in at least two essential aspects. First, Ca(>60%)Y isomerizes hexane, while silica-alumina virtually does not. Secondly, Ca(>60%)Y yields more saturated fragments. Similar cracking characteristics have been reported for the X-type zeolite catalyst (*3*).

The saturates/unsaturates ratios for C_2 to C_5 aliphatics and the iso/normal ratios

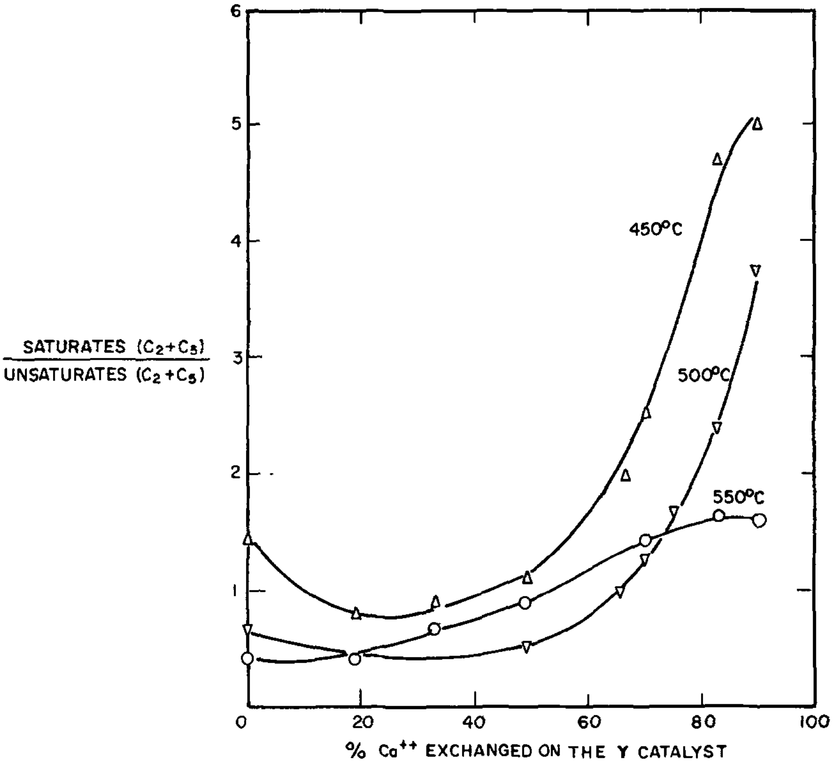


FIG. 3. Saturates/unsaturates ratios of alkanes in the reaction product.

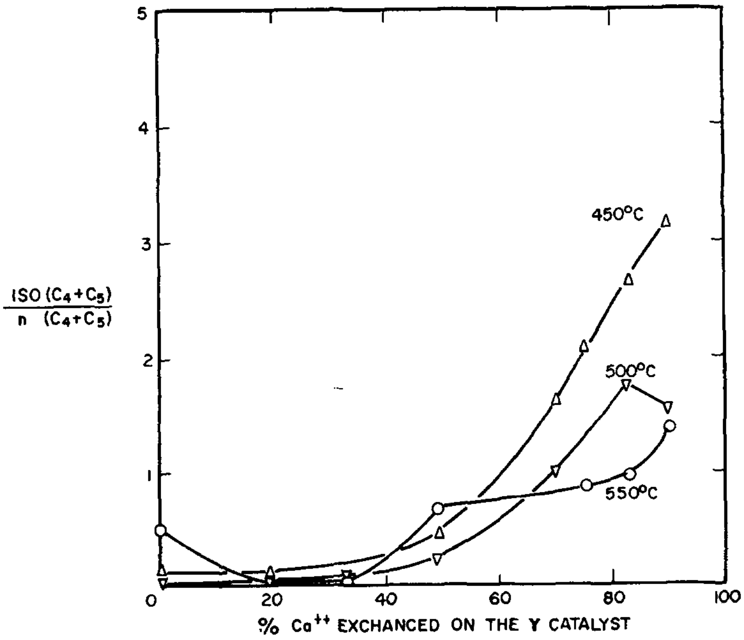


FIG. 4. Iso/normal ratios of butane and pentane in the reaction product.

for C_4 and C_5 alkanes are computed for the product gases and are plotted in Figs. 3 and 4. The turning point at around the 60% level of exchange is again exhibited by both curves. The persistence of the appearance of turning points signifies that, beyond the 60% level of exchange, a new type of catalytic activity sets in which speeds up the rates of cracking and isomerization and imparts new characteristics to the reaction product pattern. It is this new type of catalytic activity with which we shall be concerned in the following discussion.

Discussion

A. *Reactive Sites*

Three types of catalytic sites may conceivably exist on the CaY zeolite surfaces. They are Brönsted acids, Lewis acids, surface electrostatic fields.

To assume the Brönsted acids as being solely responsible for hexane cracking and isomerization would imply that the Brönsted acids on the CaY surfaces are drastically different from those on the silica-alumina surfaces. Some conventional Lewis acids, usually identified with the three coordinated aluminum ions, may exist on the broken external crystal surfaces where the crystal terminates. The population of these Lewis sites from this consideration, however, cannot be large because of the relatively small external crystal surfaces (1–2 m^2/g) and the relatively large intracrystalline pore surfaces (400–600 m^2/g) (*4*) of the zeolite crystals. Therefore, before we explore the likelihood of either Brönsted or Lewis acids functioning as reactive sites, we shall turn our attention to the cavity surface field and shall examine whether any relation exists between the field and the catalytic activity.

The origin of the cavity surface fields has been discussed at some length by Pickert *et al.* (*2*). Briefly, the Y-type zeolites, isostructural with faujasite, consist of AlO_4 and SiO_4 tetrahedra. These tetrahedra link together to form truncated cubo-octahedral cages (or cavities) of the type found in sodalite. Each cubo-octahedron possesses eight six-oxygen rings and six four-oxygen rings. Four of the eight six-oxygen rings are linked to their counterparts of the neighboring cubo-octahedra by hexagonal prisms (Fig. 5).

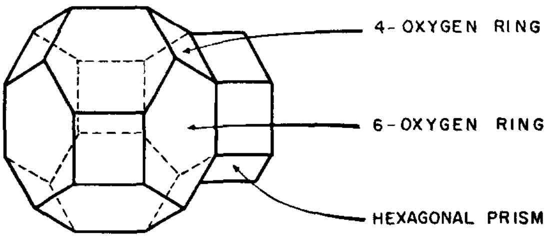


FIG. 5. Structural element of Y-type zeolite.

The cations in zeolite, necessary to balance the electrovalence of the AlO_4 tetrahedra, can exist inside a hexagonal prism (Type I site, 16 per unit cell); next to an unjoined six-oxygen ring (Type II site, 32 per unit cell); or next to a four-oxygen ring (Type III site, 48 per unit cell). A Type I site (henceforth called site I) is hidden and is inaccessible to the foreign molecules larger than 2.2 Å in diameter. Types II and III are exposed on the zeolitic surface and are easily accessible (*5*).

The NaY zeolite which we used has a structural formula of $Na_{52}(AlO_2)_{52}(SiO_2)_{140}$. The 52 sodium ions are so distributed that site I and site II are fully occupied, while site III is nearly empty (*5*). During the ion exchange and the subsequent dehydration, the calcium ions have a strong tendency to occupy site I preferentially (*2*). That is to say, in an ideal case where the preference is absolute, then of the 26 calcium ions that may replace the available sodium ions, the first 16 will enter site I.

At this point where site I is fully occupied by calcium ions (corresponds to 61% level of exchange), the unit cell will have a net lattice charge of —20,* balanced by 20 sodium ions, most of which reside in site II. Further replacement of Na^+ by Ca^{++} will set up a surface electrostatic field. This is because a Ca^{2+} ion, while replacing two

---

* A total of 52 AlO_4 tetrahedra, each of which bears a negative charge, is balanced by 16 calcium ions at site I. The net charge is therefore $-52 + 2 \times 16 = -20$.

Na^+ ions electrovalence-wise, can be physically present only near one site, thus leaving the other site empty Electrostatically, the filled site will have one net positive charge and the empty site will have one negative charge. The field strength can be quite large. Based on the ionic model, it was estimated to be several V/Å near the filled site (*6*).

From the above considerations, the inauguration of the surface electrostatic field seems to coincide surprisingly closely with the experimentally observed turning points in the rate curves (Figs. 1 and 2) and in the curves involving composition parameters (Figs. 3 and 4). This strongly suggests that the surface field could very well be responsible for the catalytic activities of the high calcium (>60%) catalysts.

B. *Reaction Mechanism*

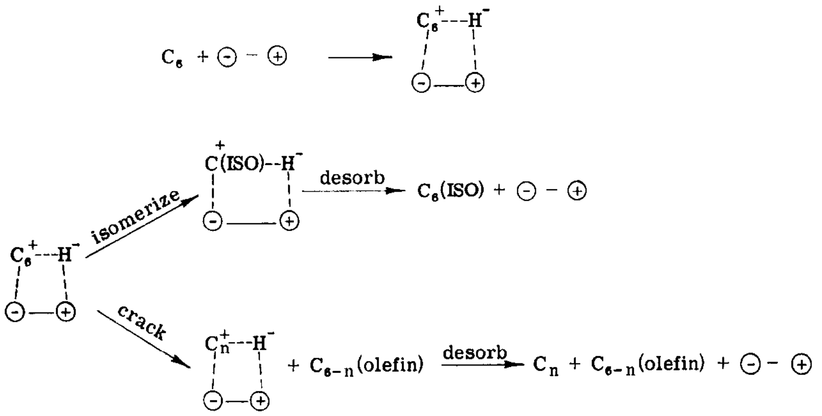
The major attributes unique to hexane cracking and isomerization over the Ca (>60%)Y catalysts may be summarized as follows:

(1) Ca(>60%)Y catalysts crack hexane at a much faster rate than the silica-alumina.

(2) Ca(>60%)Y catalysts isomerize hexane, while silica-alumina virtually does not.

(3) The reaction products possess a high saturates/unsaturates ratio for aliphatics.

These unique reaction features can be most easily explained by the conventional carbonium ion rules by assuming that the hexane molecules are sufficiently polarized (may or may not be completely ionized) by the surface field to impart to themselves ionic characteristics. In view of the high field strength present, this assumption appears plausible. For simplicity representing the field by a dipole, one may write



Here C_6 and C_6(iso) denote normal and isohexane; C_6^+ denotes $C_6H_{11}^+$; and C_n, C_n^+, and C_{6-n} (olefins) denote the paraffin, carbonium ion, and olefin with n or $6-n$ carbons in the chain when n is smaller than 6.

In contrast to the silica-alumina (*7*), the CaY can activate the hydrogen–carbon bonds through reactions (1) and (2) with fair speed. This explains attributes (1) and (2).

The high saturates/unsaturates ratio may be obtained through the above reaction paths using butene to represent a typical olefin:

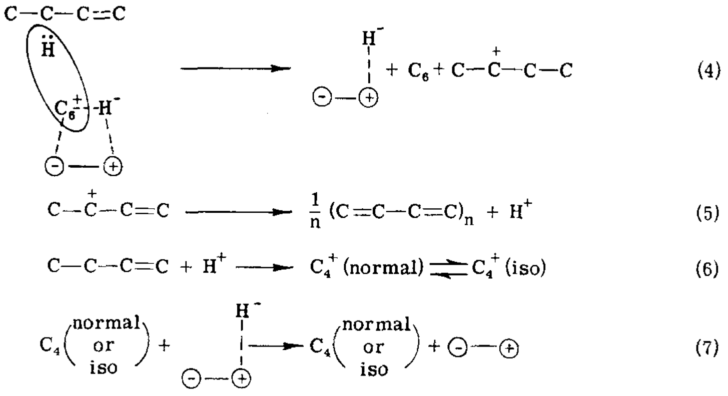
$(C{=}C{-}C{=}C)_n$ in reaction (5) can be either open-chain compounds or aromatics. In fact, a noticeable amount of aromatics was observed in the reaction product (Table 1).

C. *Ionic Diffusion and Dynamic Surface Field*

In general, a good catalyst should be capable of both activated adsorption and

---

* If cracking yields a surface-bound olefin, it could react with a proton to form a surface-bound carbonium ion. The other carbonium ion fragment will eventually decompose to yield a proton. Thus, the overall reaction shall be the same as (3).



subsequent desorption and thereby continuously promotes catalytic actions in a cyclic manner. When applied to the present case, we require that the electric field be sufficiently strong so that the hexane molecules will be polarized enough so as to bear ionic characteristics [Eq. (1)]. The difficulty arises when we also require that the same field be weak enough to allow dislodging of the reaction products [Eqs. (2) and (3)]. If one of these two somewhat contradictory requirements is not met, the reaction scheme as proposed cannot be carried forward.

This difficulty is alleviated or disappears when it is realized that here we are dealing with a dynamic system. In other words, the surface field, instead of being static, is in fact time-variant. At a certain locality, the field could be quite strong at one moment and quite weak in another. This dynamic situation arises from the fact that cations (Na^+ and Ca^{2+}) on CaY zeolite are mobile. Their mobilities can be estimated by the following equations (*8*):

$$D = \tfrac{1}{3}\lambda\nu \exp(-Q/RT) \qquad (8)$$

$$\tau = \lambda^n/nD \qquad (9)$$

where D is the diffusion coefficient (in cm^2/sec); λ, the distance between jump of the diffusion particle; ν, mean thermal velocity of the particles; Q, total energy of activation for diffusion; n, a factor depending on the geometry of the matrix; τ, average time between jumps (in seconds).

In the case of self-diffusion inside an ionic lattice, the energy of activation embodies two terms, the energy necessary to form vacancies in the crystal lattice and the energy barrier separating the original position from the neighboring sites of vacancy. In the present case, the available vacant sites on the cavity surface are numerous; and no formation of new vacancies is necessary. The total energy of activation is therefore expected to be small.

A Ca^{2+} ion conceivably can diffuse in various ways. It may jump from an occupied site II to an empty site II. It may momentarily jump from a site II to a vacant site III and vice versa. It may jump out momentarily from a site I to an empty site II, etc. When each of these movements occurs, the surface field will fluctuate. In fact, the field will fluctuate even when a Ca^{2+} ion in site I moves from one side of the prism to another. As a rough estimate, we may substitute into Eqs. (8) and (9) some reasonable figures, such as $\nu = 10^4$ cm sec^{-1}, $\lambda = 5 \times 10^{-8}$ cm, and $n = 2$, and obtain

$$\tau = 7.5 \times 10^{-12} \exp(Q/RT) \qquad (10)$$

Just to gain an impression of the order of magnitude, we may further associate each jump of Ca^{2+} ion on site II with a desorption event of Eq. (3). Under these assumptions, we obtained that, at 450°C and for a Q value of 30 kcal/mole, a τ value of 7.3×10^{-3} sec and a 0.9-g Ca(90%)Y catalyst under these circumstances will support a cracking rate of 0.075 mole/sec. Similarly, for $Q = 40$ kcal/mole, the corresponding rate of cracking is 0.75×10^{-4} moles/sec; and, for $Q = 50$ kcal/mole, 0.75×10^{-7} moles/sec. The last value is smaller than the actual cracking rate, which amounts to 1.4×10^{-6} moles/sec.* While the assumptions made here are admittedly far removed from the true situation, the computation nevertheless yields a general impression that, for a diffusional activation energy below 40 kcal/mole, the rate of Ca^{2+} diffusion is probably not the rate-controlling step of the overall cracking process.

The electrical conductivity of CaY zeolite had been measured by Freeman and Stamires (*9*), who reported an activation energy value for diffusion of around 21 kcal/mole. Whereas direct evidence of hexane polarization on zeolite is yet to be sought, interaction of hexane with CaY zeolite according to Eq. (1) is expected to decrease the surface field strength; i.e., lower the potential energy barrier of the ionic movement and thereby increase the electrical conductivity. An increase in conductivity when *n*-hexane was adsorbed on NaX zeolite indeed was observed experimentally (*10*).

---

* Feed rate 3 ml/hr, cracking 20%, see Fig. 1.

REFERENCES

1. TUNG, SHAO E, AND MCININCH, E., *J. Catalysis* 3, 229 (1964).

2. PICKERT, P. E., RABO, J. A., DEMPSEY, E., AND SCHOMAKER, V., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 714. (North-Holland Publ. Co., Amsterdam, 1965).

3. FIRLETTE, V. J., WEISZ, P. B., AND GOLDEN, R. L., *J. Catalysis* **1**, 301 (1962).

4. RABO, J. A., PICKERT, P. E., STAMIRES, D. N., AND BOYLE, J. E., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960,* p. 2055 (Editions Technip, Paris, 1961).

5. BRECK, D. W., *J. Chem. Educ.* **41**, 678 (1964).

6. RABO, J. A., ANGELL, C. L., KASAI, P. H., AND SCHOMAKER, V., *Discussions Faraday Soc.* **41**, 328 (1966).

7. HAENSEL, V., *Advan. Catalysis* **3**, 186 (1951).

8. JOST, W., *in* "Diffusion in Solids, Liquids, Gases," p. 136. Academic Press, New York, 1952.

9. FREEMAN, D. C., JR., AND STAMIRES, D. N., *J. Chem. Phys.* **35**, 799 (1961).

10. STAMIRES, D. N., *J. Chem. Phys.* **36**, 3174 (1962).