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Catalysis by Crystalline Aluminosilicates

IV. Attainable Catalytic Cracking Rate Constants, and Superactivity

J. N. MIALE, N. Y. CHEN,* AND P. B. WEISZ

From the Mobil Oil Corporation
Research Department, Central Research Division Laboratory
Princeton, New Jersey

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Crystalline aluminosilicate zeolite catalysts possessing a number of different crystal structures and ionic forms are characterized by rate constants for the cracking of *n*-hexane of from one to more than four orders of magnitude greater than the activity of conventional amorphous siliceous oxide cracking catalysts. Some are highly molecular shape selective at similarly high "superactivities." Product spectra change with the temperature at which activity is achieved. Apparent activation energies are remarkably uniform. Catalysts can now be made that span a wide range of activities, from ones that crack at conventionally high temperatures to those that approach the low-temperature performance of acid catalysts of the aluminum–hydrogen halide type.

A. INTRODUCTION

Previous reports (*1*, *2*, *3*) described the catalytic hydrocarbon cracking activity of sodium and calcium aluminosilicates of the faujasite (zeolite X) and the A-zeolite structure. It was noted that the catalytic activities were similar to or somewhat greater than those of conventional synthetic silica-alumina cracking catalysts; the behavior of the calcium form was characteristic of "acidic" catalysts. Keough and Sand (*4*) have reported on the activity of synthetic mordenite ("Zeolon") for hydrocarbon cracking. Frilette and Rubin (*5*) have demonstrated acid-activated natural mordenite to be a remarkably effective catalyst for various hydrocarbon reactions, including *n*-hexane cracking at 200°C; indications of an activity several orders of magnitude above that of conventional acidic oxide catalyst led them to compare its activity to that of HCl-promoted $AlCl_3$. The use of some forms of rare-earth-containing synthetic faujasite in gas oil cracking was described by Plank, Rosinski, and Hawthorne (*6*).

We have made a quantitative comparison of relative magnitudes of attainable cracking activities of crystalline aluminosilicate zeolites possessing a number of different crystal structures and ionic forms. A brief report was given by Letter to the Editor (*7*). This study, together with results on various aspects of behavior of a number of zeolite catalysts, will be more fully described in this paper.

B. ATTAINABLE MAGNITUDES OF ACTIVITY

1. *Conversion Measurements*

Primary data on catalytic cracking activity were obtained from measurements of *n*-hexane conversion in a Pyrex glass tube microreactor holding $V = 1.5$ ml of catalyst material of 12-28 mesh screen size or smaller. A stream of helium at a $F = 10$ ml/min flow rate was dispersed through a fritted glass disk and passed through *n*-hexane at 25°C. The saturated He-gas stream ($p_{\text{hexane}} = 0.2$ atm) was passed continuously through the microreactor, resulting in a superficial contact time, $\tau = V/F$, of $\tau = 9$ sec; this repre-

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* Paulsboro Laboratory, Paulsboro, New Jersey

sents a quite conventional magnitude of vapor contact time for catalytic cracking tests. The catalysts were initially subjected to air treatment at 538°C for 15 min prior to testing. Conversion was observed 5 min after commencement of flow by diverting a gas sample from the continuous effluent stream into a vapor-chromatographic column to obtain an analysis of products and unconverted hydrocarbon.

Conversion data were considered meaningful only between 5% and 40% of *n*-hexane conversion. Data below 5% were rejected for analytical reasons, above 40% to avoid mass and heat transport effects, and overcracking.

Because of the wide range of magnitudes of activity encountered, conversion within a limited range was obtained by making a suitable choice of reaction temperature for each sample.

An ordering of catalyst materials according to increasing activity is obtained in terms of a sequence of (decreasing) operating temperatures required to attain a similar conversion level. At a given temperature the magnitude of the rate constant is taken as the first-order constant, k, from

$$k = (1/\tau) \ln [1/(1 - \epsilon)]$$

where ϵ is the observed fractional conversion. Since we shall be discussing relative activities over a large range of *orders of magnitude*, assumption of zero or any intermediate order of kinetics within the aforementioned limited range of admissible conversion would not significantly alter the conclusions.

The derivation of constants describing magnitudes of relative activity *at equal temperature* depends on certain observed activity characteristics that will be discussed further below.

2. Catalyst Compositions

As a general reference catalyst, a conventional (commercial) amorphous silica-alumina cracking catalyst (Mobil Oil Corp.) obtained by cogelation was used (*8*). It contained 10 wt % alumina, and had a specific surface area of 420 m^2/g. Such a catalyst, having not been previously used in a cracking installation, is considered to possess a conventionally high cracking activity. It can convert about 46% of a gas oil to gasoline range hydrocarbons, as evaluated by an industrially accepted test method (*9*). Because of possible variability inherent in the use of cracking tests with complex petroleum gas oil charge stocks, we prefer to characterize the reference catalyst by its behavior in our standard microreactor measurement with *n*-hexane: It converts 12.5% of *n*-hexane passed as saturated vapor (25°C) in a stream of helium over the catalyst at 538°C, with a 9-sec superficial contact time (superficial catalyst volume/gaseous volume flow rate) at a time of 5 min after commencement of flow.

Crystalline aluminosilicates used included: Zeolite A (synthetic) and Na faujasite (synthetic) from the Linde Company; Na mordenite (synthetic) from the Norton Company ("Zeolon"); mordenite (Nova Scotia), stilbite (Halls Harbour, Nova Scotia), chabazite (Nova Scotia), and gmelinite (Bancroft, Ontario) from Wards Natural Science Establishment, Inc.; Zeolite ZK-5 synthesized by G. T. Kerr of our laboratories (*10*).

Cationic exchanges were carried out with excess aqueous solutions of ionic species as indicated in Table 1. The notation RE will refer to a mixture of rare earth ions containing about 50% Ce, 25% La, with most of the remaining 25% distributed among Nd, Pr, Sm, Gd, and Y. The anionic species was chloride.

3. Range of Activities: Effective Cracking Temperatures

The activities among the crystalline aluminosilicates tested differed by so many orders of magnitude that meaningful comparative conversion data could not be obtained at any single temperature. In each case, temperature was therefore chosen to keep conversion levels within the specified "meaningful" range.

Table 1 shows the temperature required by the zeolitic catalyst samples to obtain a cracking conversion of about 5% to 20% of *n*-hexane at similar flow conditions. A large spectrum of relative activities is evident, with appreciable *n*-hexane cracking conver-

TABLE 1

APPROXIMATE TEMPERATURE FOR OBTAINING APPRECIABLE (~5% TO 20%) *n*-HEXANE CONVERSION

Catalyst material		Major cations in exchange solution	Analysis of product (wt %)					Temperature (°C)	Alpha
Sample	Crystal structure		SiO_2	Al_2O_3	Na	Ca	RE		
1	Amorphous $SiO_2 \cdot Al_2O_3$	(Standard catalyst)						540	1.0
2	Faujasite	Ca	47.8	31.5	7.7	12.3	—	530	1.1
3	Faujasite	NH_4	75.7	23.1	0.4	—	—	350	6 400
4	Faujasite	La	—	—	0.4	—	29.0	270	7 000
5	Faujasite	RE	—	—	0.39	—	28.8	<270	>10 000
6	Faujasite	RE, NH_4	40.0	33.0	0.22	—	26.5	<270	>10 000
7	Faujasite	RE, NH_4	—	—	—	—	—	420	20
8	Zeolite A	Ca	42.5	37.4	7.85	13.0	—	560	0.6
9	Zeolite ZK5	—[a]	—	—	—	—	—	400	38
10	Zeolite ZK5	H	76.8	23.1	0.47	—	—	340	450
11	Mordenite	Ca	(~77)	—	1.01	—	—	520	1.8
12	Mordenite	Ca, H	82.0	14.0	0.4	—	—	360 to 400	40–200
13	Mordenite	NH_4	—	—	—	—	—	<270	>10 000
14	Mordenite	H	80.1	13.4	0.3	1.54	—	300	2 500
15	Mordenite	NH_4	—	—	0.1	—	—	<270	>10 000
16	Gmelinite	NH_4	—	—	—	—	—	<270(~200)	>10 000
17	Chabazite	NH_4	—	—	—	—	—	<270	>10 000
18	Stilbite	NH_4	—	—	—	—	—	370	120
19	Offretite	NH_4	—	—	—	—	—	<270	>10 000

[a] As synthesized (*10*).

sion attainable at temperatures as low as 200°C. It is of interest to examine the calculated thermodynamic capability for paraffin cracking at low temperature. Figure 1 shows the temperature required to obtain 10% to 20% conversion in the reaction *n*-hexane → propane + propene, at *n*-hexane partial pressures of 1 atm, and at 0.2 atm (as in this experimental work). Temperatures as low as 150° to 180°C are indeed seen to be thermodynamically feasible.

4. Relative Magnitude of Cracking Rate Constants

An Arrhenius plot, Fig. 2, of the observed rate constants with temperature suggests similar apparent activation energies of about 30 kcal/mole on a number of different preparations in spite of large differences in relative level of activity.

On a sample of Ca-A zeolite we have extended the study of the temperature dependence over a range of two orders of magnitude in activity. By careful and sensitive chromatographic assay of the products, the activity of this catalyst was followed downward from a conversion level of 2%. The results are shown in Fig. 3, and confirm the apparent activation energy of about 30 kcal/mole.

In another test, *n*-octane was used on a catalyst of steam-treated RE faujasite (the same type as Catalyst 7 above). Figure 4 shows the temperature dependence, which again corresponds to an apparent activation energy of 30 kcal/mole.

The occurrence of consistently similar temperature coefficients of activity suggests that a useful and valid comparison of relative rate constants, based on equal temperature, might be made: A rate constant measured at a kinetically acceptable temperature, *T*, is compared to the rate constant of a standard catalyst at the same temperature by extrapolation based on an Arrhenius plot with 30 kcal/mole temperature dependence.

Figure 5 shows a collection of rate data on some of the catalysts of Table 1, plotted to allow a direct comparison of magnitudes with the standard amorphous silica-alumina cracking catalyst. We have used "alpha"

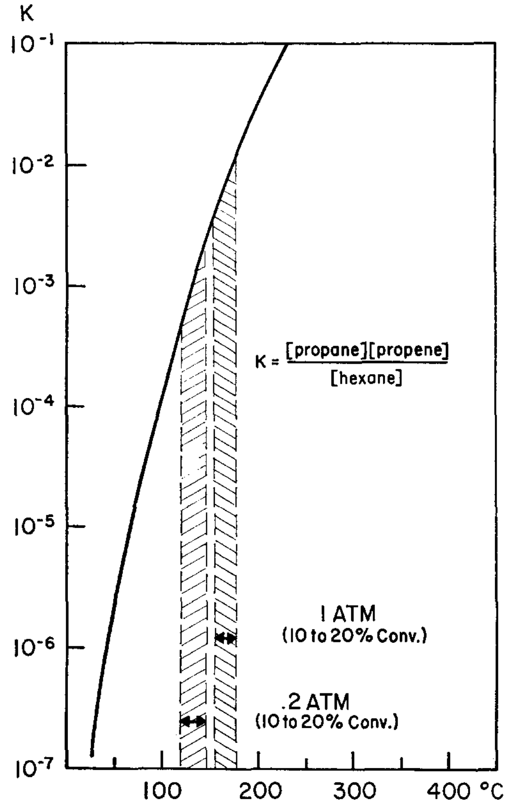

Fig. 1. Thermodynamic limitations of *n*-hexane conversion (at 1.0 and 0.2 atm *n*-hexane).

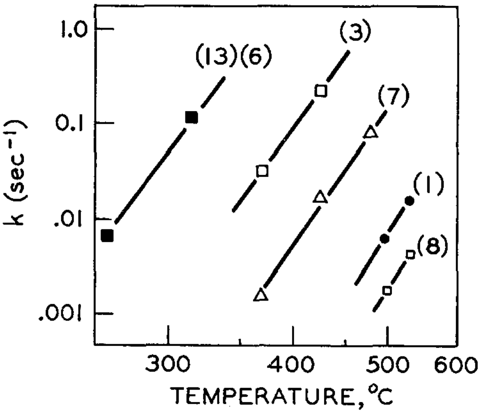

Fig. 2. Cracking activities of various crystalline aluminosilicate catalyst preparations (numbers refer to preparations in Table 1).

to represent the activity relative to that conventional catalyst. The activity of the latter is $\alpha = 1$, by definition.

Figure 5 demonstrates the procedure for derivation of alpha values for a few of the catalysts. Alpha values on all samples of Table 1 are summarized in the last column of that table. The catalysts span an activity range of more than four orders of magnitude above that of conventional amorphous oxide cracking catalysts. Superactivities of $\alpha = \geq 10\,000$ are attainable by suitable cation modification on a number of different crystal structures, as shown by examples involving faujasite, mordenite, offretite, gmelinite, and chabazite.

One can systematically choose and vary the activity level. This has been achieved, for example, by using variously severe base exchanges of Na mordenites with H^+ cations. Table 2 shows examples of mordenites that systematically span the range of possible activities.

To obtain meaningful data it is important to avoid disturbances by other phenomena: As already mentioned, operation at too high a conversion level will lead to falsification by heat and/or mass transfer phenomena. Moreover, "overcracking" leads to catalyst fouling which can be so rapid in the initial moments of operation of the "fresh" catalyst that thereafter conversion is unduly low. Conventional modes of testing, where temperature is high and measurement is based

TABLE 2

Activity of Na/H Mordenites from Na Mordenite (NaM)

Exchange preparation	Final (meq/g Na)	Alpha
2 g NaM + 100 ml (0.5 *N*) NaCl + 1.1 ml (1.0 *N*) HCl	2.3	3
2 g NaM + 100 ml (0.5 *N*) NaCl + 2.5 ml (1.0 *N*) HCl	2.1	30
2 g NaM + 100 ml (0.5 *N*) NaCl + 4.9 ml (1.0 *N*) HCl	1.8	220
2 g NaM + 100 ml H_2O + 2.6 ml (1.0 *N*) HCl	1.4	1,800
10 g NaM + 2 × 125 ml (0.1 *N*) HCl + 2 × 100 ml (1.2 *N*) HCl	0.1	>10,000

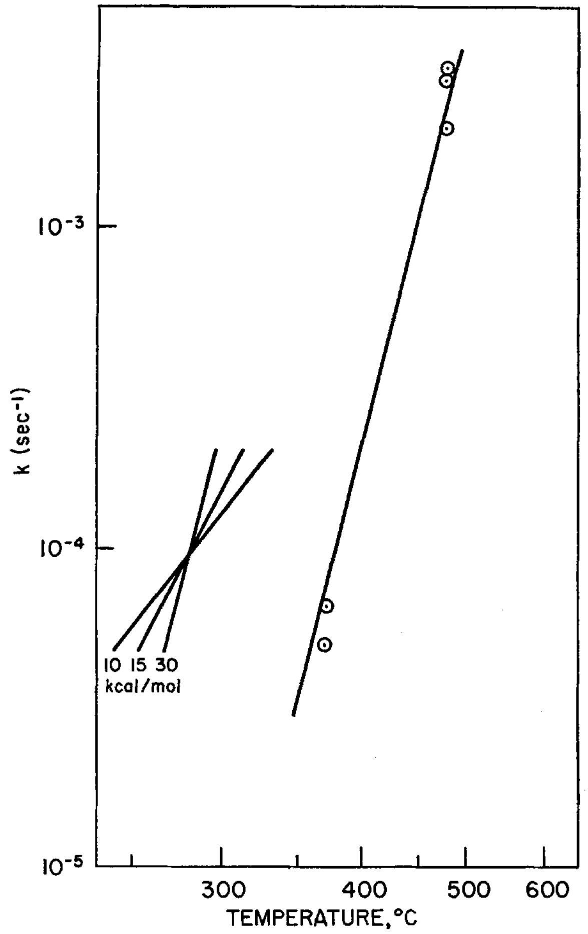

FIG. 3. Apparent activation energy for cracking of *n*-hexane over Ca-A zeolite catalyst.

on integral product accumulation over too long an interval, can therefore easily fail to reveal the superactivities as herein reported.

Operation at too low a temperature can be accompanied by hold-up and adsorption effects involving charge and/or product molecules in the early stages of operation. We therefore prefer to rely on activity data above about 300°C.

5. *Cracking of Lighter Hydrocarbons*

The available high catalytic activity can serve to crack hydrocarbon molecules smaller than hexane. Frilette and Rubin (*5*) have already reported the cracking of *n*-butane over activated mordenite. Table 3 compares results in the cracking of *n*-hexane, *n*-pentane, and *n*-butane over a synthetic H mordenite. *n*-Pentane (183 mm Hg) and *n*-bu-

TABLE 3

CRACKING CONVERSION FOR C_6, C_5, C_4, PARAFFINS OVER H MORDENITE AT 232°C

Hydrocarbon	Total conv. (%)	Cracking conv. (%)	C_1	C_2		C_3		Total C_4	Total C_5
				Par.	Ol.	Par.	Ol.		
n-Hexane	>99.0	~99.0	0.1	<0.1	0	26.8	0	71.5	0.5
n-Pentane	96.3	91.0	0.1	<0.1	0	32.8	0	58.1	—
n-Butane	44.7	14.7	0.1	0	0	14.6	0	—	5.0

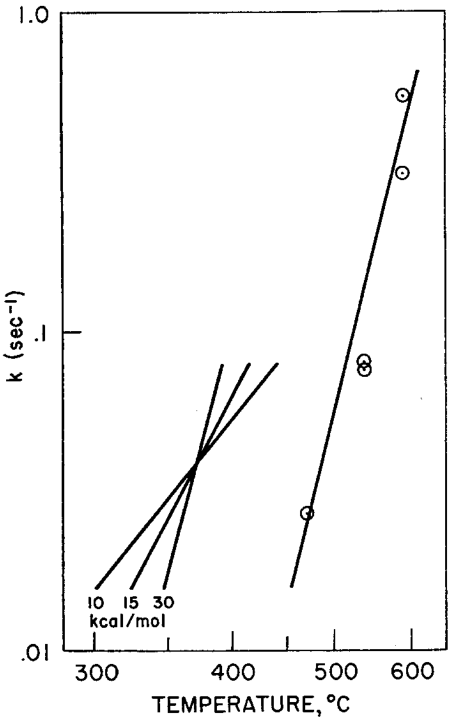

Fig. 4. Apparent activation energy for cracking of *n*-octane over a rare earth faujasite catalyst.

tane (152 mm Hg) were also carried in helium at 1-atm total pressure at conditions otherwise equivalent to the microreactor operation with *n*-hexane.

C. Shape Selectivity and Diffusivity of Zeolites

The results collected in Table 4 demonstrate the ability of offretite, gmelinite, and chabazite to yield catalysts that crack *n*-hexane with "superactivity." The data also establish the existence of intense molecular shape selectivity: Methylcyclopentane is not cracked, in spite of the exceedingly high activity for *n*-hexane conversion.

Barrer and Kerr (*11*) have indicated that there are aspherical openings with minimum and maximum effective diameters of 3.7–4.1 Å for offretite, and 3.4 to 4.1 Å in gmelinite; this is to be compared to an effective diameter of 4.3 Å in zeolite. A. Stacking faults and possibly other deviations from the ideal crystal structure are believed likely to impede effective passage through some crystallites.

The results indicate that all the materials tested have sufficient diffusivity for the *n*-hexane molecules to sustain a molecular turnover of the order of 10^{-6} moles/sec per cm^3 of the crystallites. This does not mean that diffusion inhibition of the reaction rate is negligible. Interestingly, while the zeolite A catalyst shows (Fig. 3) a normal apparent activation energy of 30 kcal/mole, we find a drastic deviation from the generally prevailing behavior for the offretite catalysts: As seen from the measurements in Fig. 6, the apparent activation energy has almost exactly one-half of the usual value. Just such a depression of the slope is expected for any situation where diffusion inhibition corresponds to a utilization factor (= Thiele modulus) $\eta < 0.5$. This indicates that the true intrinsic rate constant of these catalysts is even greater than measured. Also, if this causal reasoning is correct, the catalytic rate observation allows us to place an upper limit to the diffusivity of *n*-hexane in crystallites of the catalyst sample.

TABLE 4
Molecular-Shape Selective Cracking

Catalyst	Hydrocarbon charge	Time on stream (min)	Temperature (°C)	Conversion (%)
H Gmelinite	*n*-Hexane	10 to 33	370	47 to 30
H Gmelinite	2-Methylpentane	10 to 20	320 to 540	0 to 0.7
H Gmelinite	Methylcyclopentane	10 to 20	510 to 540	0.4 to 1.9
H Offretite	*n*-Hexane	26	320	52.1
H Offretite	2-Methylpentane	26	430	1.0
H Offretite	2-Methylpentane	26	540	4.7
H Chabazite	*n*-Hexane	30	260	10.0
H Chabazite	2-Methylpentane	10	540	1.5

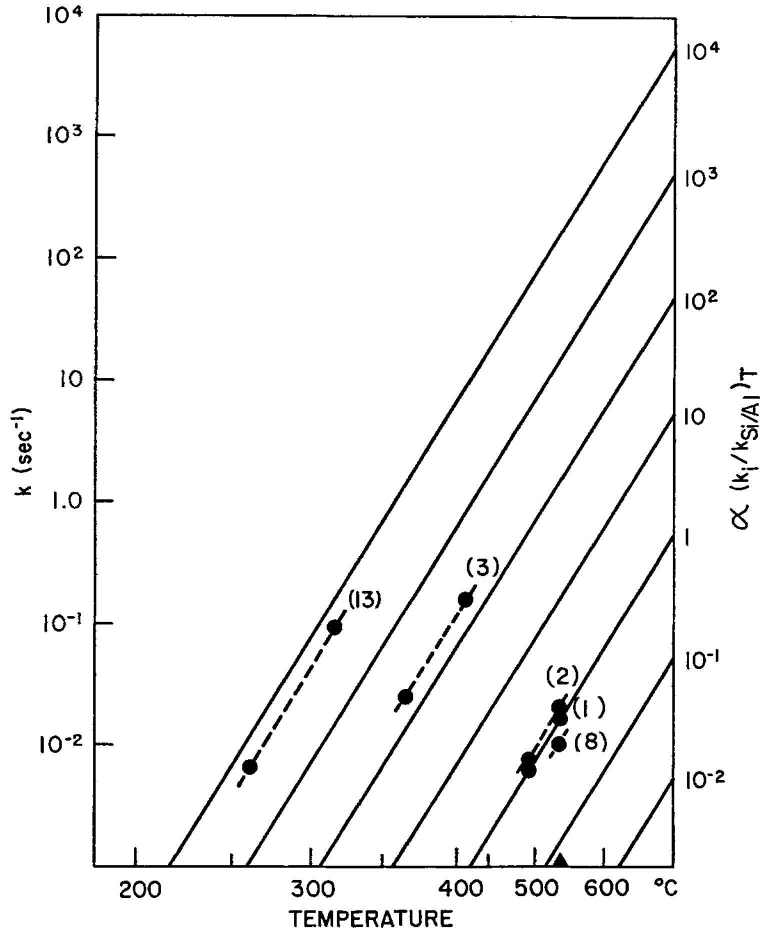

FIG. 5. Plot and procedure for determination of relative cracking activity magnitudes ("alpha").

Strong diffusion inhibition is known to result (*12*) when

$$k'(R^2/D) > 2 \qquad k' = (dn/dt)(1/C)$$

where k' is the effective, i.e., observed rate constant, and R the radius of the crystallite particles. Therefore,

$$D < \tfrac{1}{2}k'R^2$$

With rates typical of this study, $k' \approx 0.1$, and $R \approx 2 \times 10^{-4}$ cm for typical crystallite sizes, we obtain

$$D \lesssim 10^{-9}\ \text{cm}^2/\text{sec}$$

as an upper limit for the diffusivity of *n*-hexane molecules in our offretite crystallites.

This conclusion could be subjected to further study by more specific experimentation. The preliminary estimate is presented to show how *catalytic tests* may be used to derive information on the steady state molecular diffusivity of small single crystals of zeolite, since their size prohibits the use of standard methods of flow measurement.

D. Character of Products

In Table 5 we have summarized typical product patterns obtained from *n*-hexane cracking on various catalysts. The measurements were obtained at similar cracking conversions (15% to 35%).

Frilette and Rubin (*5*) have reported the production of saturated fragments in the cracking of *n*-hexane at 200°C over mordenite catalyst. Our data confirm this observation and demonstrate that this and other

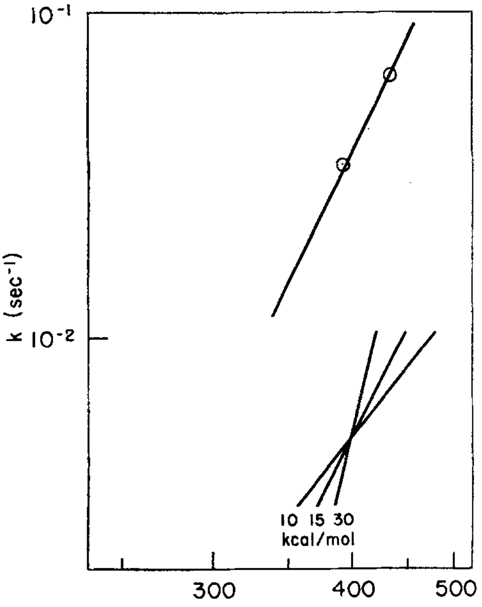

FIG. 6. Apparent activation energy for cracking of *n*-hexane over the molecular-shape-selective offretite catalyst.

product behavior is primarily characteristic of the *temperatures* at which the activity is achieved: For the various catalyst compositions capable of achieving corresponding activity levels, the propane/propene, propane/methane, and isobutane/*n*-butane product ratios are seen to rise with decreasing temperature. (Table 5 and Fig. 7a,b,c.)

The constancy of the apparent activation energy of the reaction rate over a broad range of temperatures and in spite of the large variations in the character of the reaction products suggests uniformity in the character of the rate-initiating step; but product variations result from subsequent secondary reaction processes.

Virtual absence of C_1 and C_2 products in low-temperature operation is consistent with proposed rules of carbonium ion mechanism (*13*). The appearance of such products in conventional experience has always presented special problems in the application of only the simplest of such proposed rules (*12*). Thus the implications of the simpler theory are actually approached when the investigation is conducted at lower temperatures, as is demonstrated with these catalysts.

The appearance of appreciable amounts of C_{n+1} product in the cracking of C_n hydrocarbon, when conditions are sufficiently severe to crack C_4 hydrocarbon (see Table 3), is an indication of reaction processes beyond the initial "simple" steps proposed by the elementary carbonium ion rules. This observation parallels the similar ones made by Pines and Wackher (*14*) on the aluminum halide/hydrogen halide/catalyst system for butane isomerization. A condensation–scission mechanism was proposed (*15, 16*) to account for this reaction.

The molecular shape selective catalyst (H offretite) gives a generally similar product pattern (as H mordenite, for example), except that the branched molecules (isobutane) are entirely absent. They are unable to ema-

TABLE 5

TYPICAL PRODUCT PATTERNS

Catalyst	Temp. (°C)	Total conv. (%)	Product spectrum (wt % of total converted product)								
				C_2		C_3		C_4			
			C_1	Par.	Ol.	Par.	Ol.	Par.	Ol.	(iso-C_4)[a]	C_5
Silica-alumina (amorph.)	532	12.4	4.0	1.6	8.9	18.6	55.6	3.2	7.3	(0.8)	0.8
H,Na Mordenite	482	29.4	1.6	3.3	4.9	36.9	39.3	7.4	6.6	(1.6)	<0.1
RE Faujasite	316	26.9	0.1	0.1	0.3	30.4	<0.1	43.3	<0.1	(36.8)	25.9
	371	33.5	0.3	0.5	0.9	43.8	<0.1	36.6	0.6	(27.9)	17.3
	482	27.7	1.7	0.5	4.4	48.9	29.7	6.2	5.7	(0.9)	2.9
H Mordenite	316	30.0	0.3	0.7	0.3	59.5	<0.1	29.5	<0.1	(15.4)	9.7
H Faujasite	371	17.6	0.6	2.2	0.2	47.1	6.8	24.4	1.1	(17.0)	17.6
H Offretite	260	24.0	<0.4	0.4	<0.1	37.2	0.8	37.2	1.6	<0.1	12.4

[a] Included in paraffin total.

nant from intracrystalline space and must await internal rereaction (3).

E. Summary and Conclusions

A spectrum of catalytic activity spanning over four orders of magnitude above that of a conventional amorphous siliceous oxide catalyst is available in a variety of compositions and crystalline structures of the aluminosilicate zeolites.

The gross character of reaction products moves toward higher saturation and higher branching for more active catalysts in lower temperature operation. This change is characteristic of the temperature at which the cracking kinetics are made to proceed, and is only secondarily affected by the choice of the catalyst composition.

Shape-selective catalyst species of 10 000 or more alpha activity have been obtained. Some but not all of these give evidence of intracrystalline diffusion inhibition at normal catalytic turnover rates.

These materials provide us with new capabilities for examining the cracking mechanism: With well-defined, insoluble, and permanent solid-phase catalysts for convenient mechanistic studies we can choose and control catalyst activity over a range spanning from that of conventional cracking catalysts to that of the aluminum-halide-type catalyst systems. Molecular shape selective prevention of emission of branched (or cyclic) products may become an additional tool for mechanistic research.

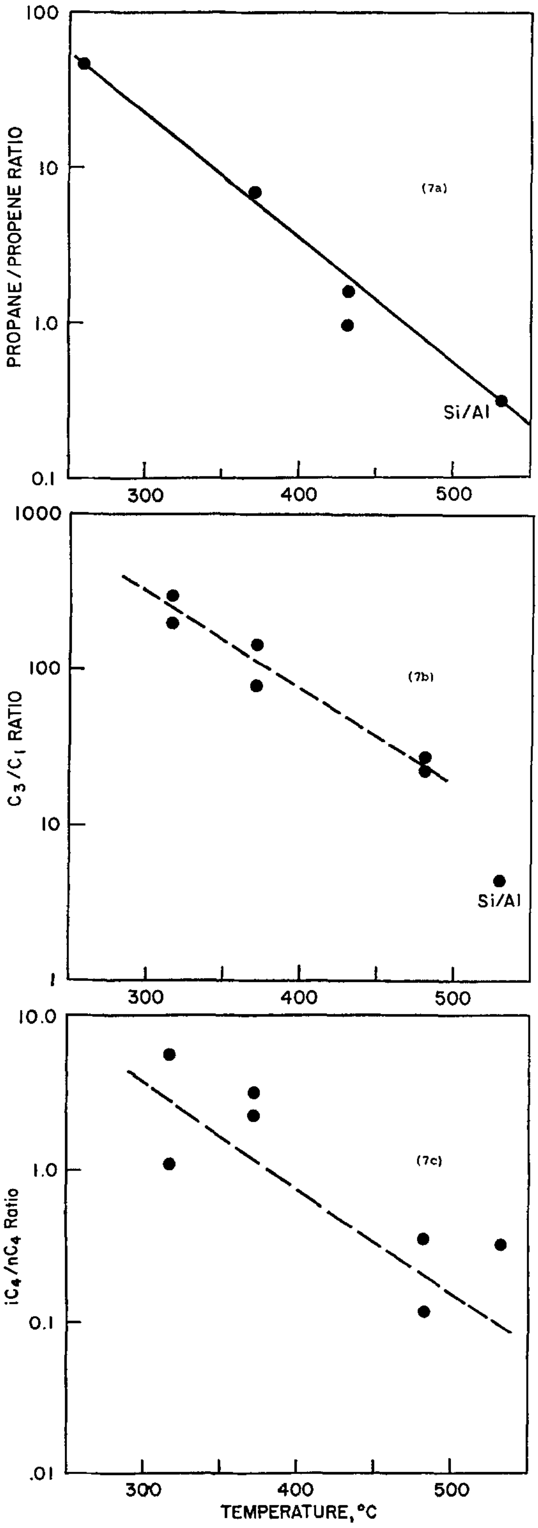

Fig. 7. Variation of the product ratios propane/propene (a), propane/methane (b), and isobutane/butane (c), for *n*-hexane cracking on a variety of catalysts.

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