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A New Concept in Zeolite-Catalyzed Reactions: Energy Gradient Selectivity

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A study of the cracking of *n*-heptane, *n*-octane, and isooctane on a variety of zeolites (erionite, offretite, ZSM-5, mordenite, and faujasite) has shown that the formation of light products (C_1, C_2, C_3) is favored for zeolites with small cavities or tortuous channels (erionite, highly decationated offretite, and ZSM-5). The C_4 production is kept high when molecules have access only to rather large channels or cavities (cationic offretite, mordenite, and faujasite). It is proposed that the occurrence or not of secondary reactions, which determines the ratios C_4/C_3 and C_4/C_2, depends on an "energetic" selectivity which characterizes cages or channels. The smaller and the more tortuous is the space where the molecules move, the higher are the field and field gradient and the more are secondary reactions favored. The ratio C_4/C_3 (or C_4/C_2) is proposed as an "energy gradient selectivity" index. This index does not depend on factors which are related to shape selectivity. © 1985 Academic Press, Inc.

INTRODUCTION

Selectivity in the catalytic transformation of hydrocarbons over zeolites in a major parameter for the industrial use of these catalysts. Two main types of selectivity can be identified. One, studied in great detail during the past decade, is related to the respective geometry of the cages and of the molecules (reactant or products). This is "shape selectivity" (*1*). The other type, which is well recognized but not so well defined, results from the chemical influence experienced by the molecules in the cages. It is related to the crystal field in the cavities and Rabo has referred to it as the polarizing power of the zeolites (*2*). This type of selectivity could be called an "energy gradient selectivity," by contrast with the first type which is purely geometric. In many cases both selectivities will direct the product distribution. In some zeolites, such as ZSM-5, shape selectivity prevails when bulky molecules are considered (branched hydrocarbons or alkyl aromatics), while with large pore zeolites (Y, for instance) the energy gradient selectivity will be the more important. The first type of selectivity can be studied using geometric considerations. The second one is not very easy to characterize quantitatively. This paper presents an approach to such characterization, using mainly linear paraffin molecules as examples in order to avoid steric hindrance effects.

EXPERIMENTAL

Catalysts. Erionite zeolites from Union Carbide, referred to as SK 15E, with formula $Na_{4.7}K_{2.0}H_{0.8}(AlO_2)_{7.5}(SiO_2)_{24.5}$ and from Société Chimique de la Grande Paroisse with formula $Na_{2.5}K_{4.7}H_{0.4}$ $(AlO_2)_{7.6}$ $(SiO_2)_{24.4}$, have been exchanged in order to obtain samples with various proton and K^+ contents (Table 1). A series of variously exchanged offretites (*3, 4*) was previously obtained from a TMA offretite sample provided by Barrer (*5*) for which the chemical composition was $Na_{0.07}K_{3.1}TMA_x(AlO_2)_{3.6}$ $(SiO_2)_{14.4}$ (TMA: tetramethylammonium). Samples of mordenite $[Na_{0.47}H_{7.53}(AlO_2)_8$ $(SiO_2)_{40}]$, Y faujasite $[Na_{7.5}H_{48.5}(AlO)_2)_{56}$

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TABLE 1

n-Heptane Cracking (H_2) at 723 K: Conversion and Product Formation (%)

Catalysts	Cation exchange for proton (%)	Conversion (%)	C_1	C_2	C_3	iso-C_4	n-C_4	C_5+	C_4/C_3[a]	Deactivation[b] (%)
Erionite	78	11	2	10	50	0	30	8	0.6	82
	64	7	2	11	50	0	29	8	0.58	36
	5	1	1	11	49	0	29	10	0.59	[c]
ZSM-5	95	31	1	11	45	10	27	4	0.82	16
Offretite	83	13	1	4	45	21	26	3	1.04	35
	72	7	1	5	43	21	24	6	1.05	12
	32	1	2	5	40	22	26	5	1.2	10
Mordenite	94	3	1	3	42	24	25	5	1.16	90
HMgY	40	8	1	3	39	24	25	8	1.26	75

[a] C_4/C_3 values measured after 2 hr on stream. In all cases, a slight increase within 10% of the initial C_4/C_3 values is noted after 15 hr on running.

[b] Calculated by comparing initial activity and remaining activity after 15 hr on stream.

[c] Not determined.

$(SiO_2)_{136}$ and $Na_{5.1}Mg_{13.3}H_{24.3}(AlO_2)_{56}(SiO_2)_{136}$], and ZSM-5 [$Na_{0.2}H_{2.64}(AlO_2)_{2.85}(SiO_2)_{93.15}$] have also been used.

Prior to any catalytic experiments, all zeolite samples have been activated by a similar heat treatment at 550°C under dry air flow, followed by a hydrogen sweep *in situ* at 450°C for 15 hr.

Catalytic experiments. Catalytic experiments were performed in a dynamic microreactor connected to an automated system of gas chromatographic analysis. n-Octane, n-heptane, and isooctane (trimethyl-2,2,4-pentane) conversions were carried out in flowing hydrogen in the following experimental conditions: flow rate = 2.4, 2.4, 2.8 liters/hr; reaction temperature = 723, 723, 738 K; partial pressure ratio P_{HC}/P_{H_2} = 0.06, 0.06, 0.15, unless otherwise specified.

The weight of zeolite material used in each catalytic experiment was adjusted in order to avoid conversions higher than 10% and to prevent any channeling effect in the catalytic bed. In order to compare the various zeolites, tables give the percentage of conversion for a unit weight of catalyst (chosen as 100 mg). This may result in calculated values higher than 10%. Product distributions are detailed from C_1 to C_4 hydrocarbons, all the heavier gaseous products being referred to as C_5+.

Catalytic reactions were also performed in a Sartorius thermobalance under either hydrogen or nitrogen atmosphere in order to follow the coke deposition and to relate it to the deactivation. These experiments were performed in dynamic conditions, close to those used for the catalytic tests in microreactor. Occasionally a chromatographic analysis was coupled with the thermobalance experiment in order to establish firmly the relation between the gain of weight and the catalytic performance.

RESULTS AND DISCUSSION

Important changes in selectivity are obtained when moving from one zeolite to another. Due to the size of their pore aperture, erionite samples do not give branched products. For all the zeolites concerned, C_3 and C_4 are the major products. The C_5+ products are formed in larger amounts with erionite samples. Looking more precisely to the C_1 to C_4 products, it is observed that zeolites can be ranked such that the production of light hydrocarbons C_1 to C_3 decreases while that of total C_4 (iso- and n-) increases, irrespective of whether n-hep-

TABLE 2

n-Octane Cracking (H_2) at 723 K: Conversion and Product Formation %

Catalysts	Cation exchange for proton (%)	Conversion (%)	C_1	C_2	C_3	iso-C_4	n-C_4	$\frac{\text{iso-}C_4}{n\text{-}C_4}$	C_5+	C_4/C_3[a]
Erionite	78	10	2	12	38	0	42	0	6	1.1
	64	8	2	10	34	0	44	0	10	1.3
	5	1	1	9	33	0	44	0	13	1.3
ZSM-5	95	25	0.5	4	43	16	30	0.5	7	1.1
Offretite	83	22	2	8	37	19	28	0.7	6	1.3
	53	5	3	6	35	18	30	0.6	8	1.4
	32	3	1	4	28	21	40	0.5	6	2.2
	11	1	1	2	27	24	46	0.5	ε	2.6
Mordenite	94	12	1	6	27	25	38	0.7	3	2.3
HNaY	93	4	1	4	30	26	37	0.7	2	2.1
HMgY	40	20	2	3	26	33	34	1.0	2	2.6

[a] After 2 hr. A 10–15% increase of the C_4/C_3 initial values is noted after 5 hr on stream.

tane, n-octane, or isooctane is used (Tables 1, 2, and 3). The reaction mechanisms which lead to such similar trends for the three paraffins on a large variety of zeolites cannot be easily established due to all the possible side reactions. Nevertheless, the experimental evidence suggests that the trend is meaningful and that it characterizes some zeolite property. It can be expressed by various ratios, for instance, C_4/C_2 or C_4/C_3. In what follows the ratio C_4/C_3 will be used, but the conclusions reached would be similar using C_4/C_2. In a simpler cracking reaction (n-hexane) the same C_4/C_3 ratio was used to localize the primary scission of the molecule in the primary cracking step (*6*). The C_4/C_3 ratios obtained after 2 hr on stream in the n-heptane and n-octane cracking are reported in Tables 1 and 2. They increase in the order: erionite < ZSM-5 < offretite < mordenite < faujasite. The changes with cation exchange percentage in erionite and offretite will be discussed in greater detail in what follows. For any zeolite, it was observed that the initial C_4/C_3 values were slightly increased with time on stream. After 15 hr they rose by about 10%. Catalyst deactivation proceeds simultaneously and Table 1 reports the percentage deactivation after 15 hr. No correlation is noted between the extent of aging and the C_4/C_3 ratio sequence. A more detailed study of offretite and erionite deactivation will now be discussed.

TABLE 3

Isooctane Cracking (H_2) at 738 K: Conversion and Product Distribution (%)

Catalysts	Cation exchange for proton (%)	Conversion (%)	C_4/C_3
Erionite	78, 64, 5	0	—
Offretite	83	9	1.2
	32	1	4.7
	12	1	7.6
Mordenite	94	16	8.0
HNaY	93	4	7.0
HMgY	40	11	10.0
HKY	85	2	13.2

I. Offretite and Erionite

These zeolites have been studied more extensively because they have similar structures but show different C_4/C_3 ratios. Moreover, offretite shows a dependence of this ratio upon ion content while erionite does not (Tables 1 and 2).

A. Particle size. It is well known that shape-selective catalysis is more and more efficient as the particle size increases (*1*). The C_4/C_3 ratio changes observed in this study could therefore be due to that effect. An electron microscope study (*7*) showed that erionite appears as monocrystalline long fibers (along 001 axis) whose length is usually about 3.5 μm. Offretite monocrystalline particles are rice-shaped, and their most frequent length is 0.6 μm. The study did not detect any significant change in shape or size upon cation exchange of either erionite or offretite. Therefore the selectivity changes observed with offretite at various ion exchanges cannot be ascribed to changes in particle size.

B. Influence of coke. Besides the decrease in catalytic activity due to coking it is well accepted that selectivity changes may occur upon coke deposition. First, side reactions may lead to the consumption of some primary products acting as coke precursors. Second, coke deposits have been shown to restrict the diameter of the pore through which the molecules diffuse in ZSM-5, increasing the shape-selective effect (*1*). It was thus important to undertake a thorough study of the C_4/C_3 ratio change as a function of zeolite deactivation.

Figure 1 reports *n*-heptane cracking on offretite-83 as a function of the time on stream. It shows no direct correlation between the deactivation which follows the gain in weight due to coke deposition as measured in a thermobalance in nitrogen atmosphere and the C_4/C_3 ratio which is kept almost constant after a slight increase in the first 2 hr. The ratio is therefore not dependent on either the extent of conversion or on the amount of coke in the zeolite channels. Regarding the olefin/paraffin selectivity which is illustrated by the propene/propane ratio, a marked decrease in the first period of the run is followed by a slow increase up to a stable value after several hours on stream. This parallels very closely the rate of deactivation and of coke formation, the latter being identified by the gain in weight (Fig. 1, curve a) or the carbon balance deficiency (Table 4). This is quite consistent with the known role of olefinic products in the coke formation process (*8*). Again, however, no straightforward correlation is noted between these olefin/paraffin changes and the C_4/C_3 ratio. Values taken after 3 min or 15 hr on stream for erionites and offretites and reported in Table 4 show that in any case the C_4/C_3 ratio is lower and not much dependent on ion content with erionite and it decreases at high proton content with offretite. No correlation is observed at all either for erionite or offretite with the conversion level, with the total amount of coke deposited or with the weight of coke formed per acid site, even after 15 hr when the carbon balance reaches 100%. The independence from coke deposition is not in line with what is usually observed in shape-selectivity catalysis. The ratio only depends on the zeolite type and, with offretite, on the cation-exchange level.

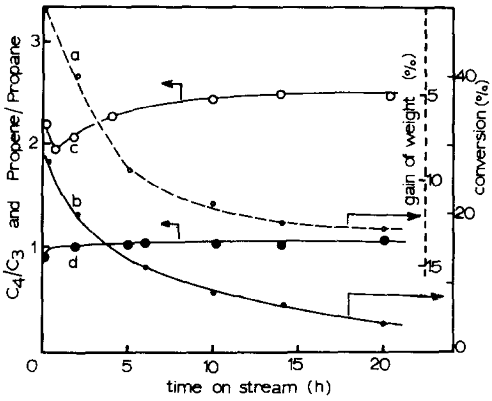

FIG. 1. *n*-Heptane cracking at 723 K on offretite-83 versus time on stream. (a) Gain of weight (dotted scale on the right), (b) *n*-heptane conversion (solid scale on the right), (c) propene-to-propane ratio, (d) C_4-to-C_3 ratio.

Simultaneous *n*-octane cracking and changes in weight on erionite and offretite samples gave the results reported in Fig. 2. The figure shows that under a hydrogen gas flow erionite-78 and offretite-72 with similar cation-exchange levels deactivate similarly with regards to weight gain and activity loss. The product distribution, very similar to the related values in Table 2, indicates no

TABLE 4

n-Heptane Cracking on Erionite and Offretite (T = 723 K)

Catalysts	After 3 min on stream			After 15 hr on stream				
	Conversion (%)	C_4/C_3	Carbon balance (%)	Conversion (%)	C_4/C_3	Carbon balance (%)	Amount[c] of coke (wt%)	g coke per acid site[c]
Erionite								
78[a]	60	0.62	81	5.5	0.81	102	9	9.7
64	19	0.63	[b]	4	0.75	[b]	[b]	[b]
5	7.5	0.7	99	0.2	0.75	100	0.9	18.0
Offretite								
83	28	1.05	79	6	1.08	101	12.4	12.4
72	18	1.05	[b]	6	1.11	[b]	[b]	[b]
32	7	1.22	[b]	0.2	1.36	[b]	1.5	5.2

[a] Percentage cation exchange for protons.
[b] Not determined.
[c] Nitrogen atmosphere.

drastic difference between the two zeolites except of course the absence of iso-hydrocarbon in the erionite products. Figure 2 also reflects very close C_4/C_3 ratios. When the catalytic reaction is carried out under nitrogen a much more severe deactivation occurs (Fig. 2f) and the rate of coke deposition is about 15 times higher than the rate observed in the hydrogen atmosphere (Fig. 2g). This could be related to the known hydrogenating properties of some zeolite catalysts. The C_4/C_3 ratios are similar in hydrogen or nitrogen atmosphere within the experimental error (Figs. 2a–b). Experiments were also carried out with the offretite-32 sample which gives in n-octane cracking (microreactor) a high C_4/C_3 ratio (Table 2). The weight gain was very small under hydrogen. Due to the low catalytic activity no detailed selectivity results could be obtained in the thermobalance experiments. The C_4/C_3 ratio could nevertheless be calculated. Its value (2.1) is very close to that obtained in the microreactor (2.2) and did not depend on the time on stream.

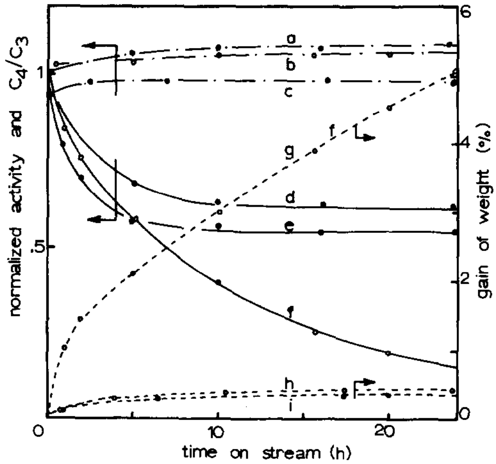

FIG. 2. n-Octane conversion at 723 K versus time on stream in flowing H_2 or N_2 atmosphere in thermobalance. (a, b, c) C_4-to-C_3 ratio; (d, e, f) normalized conversion; (g, h, i) gain of weight. Catalyst samples: (a, e, h) offretite-72 in H_2 atm, (b, f, g) offretite-83 in N_2 atm, (c, d, i) erionite-78 in H_2 atm.

To sum up, neither for n-heptane nor for n-octane cracking, does the C_4/C_3 ratio vary with the degree of conversion or with the amount of coke deposited either during a run or due to the absence of hydrogen in the atmosphere. This ratio is therefore not dependent upon pore size or geometric constraints.

C. Effect of molecule size or degree of saturation. The observation of similar C_4/C_3 ratios changes both with a linear paraffin (n-heptane or n-octane, see Tables 1 and 2) or with a branched paraffin (isooctane, see Table 3) does not suggest any correlation with the shape of the reactant molecule.

The linear hydrocarbons C_3 and C_4 have very similar dimensions. The kinetic diameters of propane and *n*-butane are 4.3 Å and their diffusion coefficients in the selective potassium T zeolite are similar and close to 3×10^{-12} cm^2 sec^{-1} at 573 K (*9*). Thus, at least for these two paraffins, mass transport or steric inhibition will not operate in selectivity changes. No detailed values are known for the diffusion coefficients of the various olefins, and some discrepancies in C_4/C_3 ratios may arise from these hydrocarbons or from branched molecules. In fact Table 5 clearly shows that the C_4/C_3 ratio does not depend on changes in the distribution of the C_4 products obtained whether they are saturated or not, or branched or not. For example, similar C_4/C_3 ratios are obtained with erionite and highly exchanged offretite in spite of the fact that erionite does not give isomolecules. Hence no correlation is observed between the C_4/C_3 ratio changes and the presence or disappearance of given C_4 molecules which would regulate selectivity. It may be concluded that the systematic low values of the C_4/C_3 ratio which are observed with the same erionite and offretite zeolites in *n*-heptane and *n*-octane cracking cannot be assigned to a shape selectivity effect coming from a phenomenon of inhibition in the mobility or in the structure of a molecule.

It follows from this that the C_4/C_3 ratio cannot be related to geometric effects as in shape-selectivity catalysis. It is suggested that it is rather related to an energetic selectivity and depends on the forces experienced by molecules in the cavities they enter.

D. Effect of cation content: Acidity and cage accessibility. A previous study on isooctane cracking on offretite showed that the isooctane conversion level parallels the strong protonic acid sites amount while the selectivity depends only on whether the catalystic reaction occurs in the channels or in the gmelinite cavity (*4*). The changes in acidity of erionite (*3*) and offretite (*4*) with cation content are very similar to each other, i.e., the strong acid sites are formed at high exchange level (>80% cation exchange). *n*-Heptane and *n*-octane cracking are both greatly increased at high cation exchange on the two zeolites. This suggests that, as with isooctane on offretite, the percentage conversion depends on the number of strong acid sites. By contrast, two distinct behaviors are observed for selectivity.

(i) On offretite, sharp and opposite changes in the percentage of C_4 and C_3 products formation occur at intermediate cation exchange (between 30 and 60%) as exemplified in Fig. 3 for the cracking of *n*-octane (curves a–b) and isooctane (curves c–d). This led us to assume that for those cases the C_4 and C_3 opposite changes result from the cage accessibility to reactants and

TABLE 5

n-Octane Cracking (H_2) at 723 K: C_4 Product Distribution (%)

Catalysts	Cation exchange (%)	Isobutane	Butane	Isobutene	Butene	*trans*-Butene-2	*cis*-Butene-2	C_4/C_3
Erionite	78	0	32	0	18	29	21	1.1
ZSM-5	95	17	35	17	4	12	15	1.1
Offretite	83	19	19	21	9	15	17	1.3
	32	9	17	26	10	20	18	2.2
Mordenite	94	14	18	25	10	16	17	2.3
HMgY	40	42	15	7	3	6	27	2.6

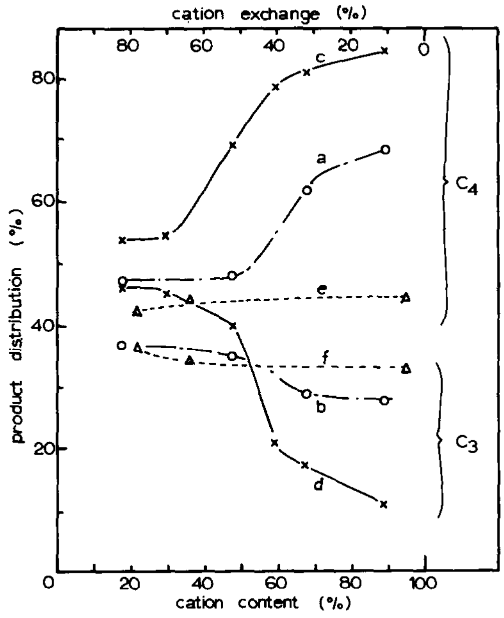

FIG. 3. Changes in product distribution versus cation content for offretite (a, b, c, d) and erionite (e, f) in *n*-octane (a, b, e, f) and isooctane (c, d) cracking.

not from the presence or absence of strong acid sites. Hence the hypothesis already given for isooctane (*3*, *4*) seems to be valid for the linear paraffins considered here. At high cation content, the molecules move only in the channel ($\phi \sim 0.63$ nm) and the hydrocarbon molecule is cracked in this rather large space. When the ion content is lower than 2.5 K/unit cell (cation exchange > 30%) the hydrocarbon may move through the gmelinite cavities (aperture 0.36 × 0.52 nm) which have then two windows free of cations. At cation exchange higher than 60%, the three windows of the gmelinite cavity are free of cations and the hydrocarbons move in three dimensions. The C_4/C_3 ratio then is decreased when besides molecules moving freely in linear channels some of them are trapped in cavities which they enter through a tortuous way of movement (see Fig. 4, left part).

(ii) No C_4/C_3 ratio changes occur on erionite whatever the exchange level, whether *n*-heptane or *n*-octane are considered (Fig. 3e–f). For erionite, the only accessible part of the structure is made of erionite cavities 1.3 × 0.63 nm closed by 8-membered rings (0.36 × 0.52 nm). Due to the well-known "window effect" the C_7 to C_9 paraffins whose dimensions are close to those of the cage are entrapped in the cavity where they are cracked to small fragments (*9*, *10*). Inferentially, in erionite the tortuous movement of hydrocarbon molecules from one cavity to the next is the only one which operates at any ion content, as illustrated in Fig. 4 (right part), giving a low and invariant C_4/C_3 ratio.

Hence, the low C_4/C_3 ratio will be typical of tortuous flow of molecules (erionite and decationated offretite) and the high C_4/C_3 ratio will be typical of rather free or linear flow (cationated offretite). The formation of light molecules (C_1 to C_3) can be reasonably explained by a cracking giving more secondary reactions when the molecules have to jump from one small cavity to the next instead of moving in a large linear channel. Going from one potential well to another through the potential barrier of a narrow aperture will disturb the molecule much more than when it flows smoothly in the rather homogeneous field of a large channel (*11*).

II. Generalization to Other Zeolites

Applying the above ideas to the other ze-

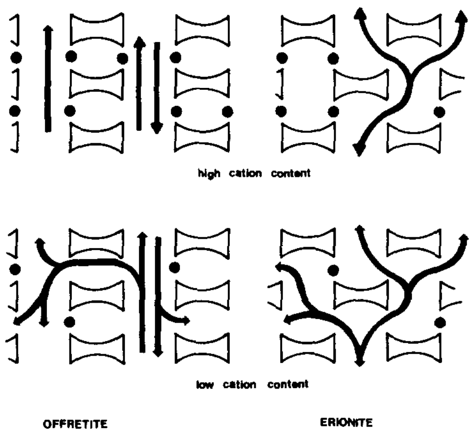

FIG. 4. Types of movement of molecules through offretite and erionite structures as a function of the cation content.

olites considered in the study can greatly help in the understanding of the changes in the C_4/C_3 ratios obtained. General features which were evidenced with offretite and erionite are also observed with the other zeolites described here.

(i) The sequence of average particle size is offretite $\sim$ ZSM-5 (0.6 μm) < faujasites (1 μm) < erionite (3.5 μm), which does not follow the C_4/C_3 series in Tables 1, 2, and 3.

(ii) The deactivation after 2 hr on stream in *n*-heptane cracking (Table 1) is not connected with the C_4/C_3 ratio. For instance, erionite-78, mordenite, and HMgY give high deactivation but different C_4/C_3 ratios. This ratio cannot therefore arise from the specific consumption of a compound giving coke precursors. Deactivation studies coupled with weight-gain experiments were performed. As with erionite and offretite, the C_4/C_3 ratio does not change much with time on stream. For instance, *n*-octane cracking on ZSM-5 gives an initial C_4/C_3 ratio of 0.9 which increases slightly up to a constant value of 1.1 after 2 or 3 hr in a manner similar to what was reported in Fig. 1 for *n*-heptane/offretite while the deactivation proceeds. Similar behavior of mordenite and faujasite show that the ratio does not depend on the presence of coke.

(iii) For none of the zeolites in Tables 1, 2, and 3 can the C_4/C_3 ratio be linked to the extent of conversion. It is also independent of the distribution of the C_4 products between branched or linear paraffins or olefins (Table 5).

(iv) It does not seem either that the identity of the cation can induce specific C_4/C_3 values at least for *n*-paraffins.

It turns out that ZSM-5, which contains some Na^+ cations, does not behave in a very singular way by comparison with highly exchanged erionite and offretite which contain K^+ ions. In contrast, its selectivity is different from that of Na mordenite or HNaY. The Mg^{2+} ions in MgHY do not either give a specific C_4/C_3 ratio. This agrees with results obtained in a study of isooctane cracking on NaHY, KHY, CaHY, LaHY, and HKL zeolites and giving high C_4/C_3 ratios for any of those cations (*12*).

As for offretite and erionite one can then consider the characteristics of the cages or channels where the molecules have to travel, in order to explain the C_4/C_3 ratios. In an attempt to classify the observations, Table 6 reports for the various zeolites the geometric dimensions of the pore systems, the C_4/C_3 ratios in *n*-octane cracking and the molecule movement type. This latter is described by two limiting cases. The first

TABLE 6

Correlation of the C_4/C_3 Ratio in Products of *n*-Octane Cracking with Characteristic Properties of Zeolites Used as Catalysts

Zeolite	Pore type	Cage size (nm)	Aperture (nm)	C_4/C_3 (*n*-octane)	Energy environment	
					Heterogeneous	Homogeneous
Erionite	Cage	1.3 × 0.63	0.36 × 0.52	1.1 to 1.3	×	
ZSM-5	Channel		0.54 × 0.56	1.1	×	
	Channel		0.52 × 0.58			
	Intersection[a]	~0.9				
Offretite	Gmelinite Cavity	0.65 × 0.78	0.36 × 0.52	1.3 to 1.4	×	
	Channel		0.63	2.2 to 2.6		×
Mordenite	Channel		0.67 × 0.7	2.3		×
Faujasite	Interconnected Cavities	~1 to 1.3	0.74	2.1 to 2.6		×

[a] See Ref. (*14*).

one referred to as "heterogeneous energy environment" occurs when molecules diffuse in narrow channels or from small cages to small cages through small windows, i.e., from a space of high field to another one through high potential barriers (high-energy gradient). The second one ("homogeneous energy environment") describes molecules moving in channels with very open cages or from large cages to large cages through large windows, i.e., in a space with small field gradient. The erionite cavity in erionite, the gmelinite cavity in offretite and channels in ZSM-5 would give rise to the first class while, due to their size and shape, channels in offretite and mordenite and the three-dimensional supercage network in faujasties will be related to the second type. Table 6 shows a correlation between the two classes of molecule movement as defined above and the C_4/C_3 ratios. It will give the same relationship if C_4/C_2 ratios are used.

Therefore, the hypothesies already proposed for offretite and erionite on the importance, for C_4/C_3, of the molecule movement type appears to be a general guideline. In *n*-heptane, *n*-octane, and isooctane cracking it relates the selective formation of light products C_2 and C_3 over those in C_4 to the access of molecules in small cages or narrow channels. The molecules entering small cavities or tortuous channels are cracked into smaller fragments than molecules which are free in large cavities or linear channels, probably due to the high zeolite field and high field gradient. This "energy" effect is related to the location of active sites in the structure and to the energetic environment where the molecules have to travel to reach the sites. It has to be pointed out that the energy or field gradient influence is dependent not only on the geometry of the distribution of potential charges which generate the field in the cages but also on the number of charges and therefore on the actual energy map. For instance, one can expect that changes in the Si/Al ratio of a given zeolite structure which modify the charge density should change the C_4/C_3 values. This was in fact observed in a comparison of Y and X zeolites in isooctane cracking. The C_4/C_3 ratio was about twice as much with the X type (*12*). Similarly the C_3 gas yield was shown to increase with the framework Si/Al ratio (*13*) in ultrastable faujasites. A decrease in C_4/C_3 corresponding to higher field gradients in zeolites (high Si/Al) is in line with what is expected at those low aluminum contents.

CONCLUSION

The study provides an explanation of the changes in C_4/C_3 (or C_4/C_2) ratio for a large series of different zeolite structures. The relation with the movement of molecules in an environment of heterogeneously distributed energy is an attempt to quantify a type of selectivity due to energetic parameters. The experimental C_4/C_3 (or C_4/C_2) ratio can be considered as an "energy gradient selectivity index" which evaluates the field effect. This could be used as a probe for the prediction of the presence of small cages or tortuous channels in an unknown zeolite structure. Such an approach is also valuable in an industrial context since the C_4/C_3 values which can be calculated from results with FCC (fluid catalytic cracking) units (*15*) are in line with the present results and can therefore be explained on the same basis. A high field gradient in zeolites is responsible for the high yield of light products.

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