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The Energy Gradient Selectivity Concept and the Routes of Paraffin Cracking in FCC Catalysts

Gabriela de la Puente and Ulises A. Sedran[1]

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ,UNL-CONICET), Santiago del Estero 2654, (3000) Santa Fe, Argentina

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The conversion of *n*-hexadecane over steam dealuminated and equilibrium FCC catalysts of different types, containing Y zeolite, was studied in a discontinuous fluidized bed reactor at different reaction temperatures in the range of 440–550°C and contact times from 1 to 60 s. The analysis of product distributions following the approach of energy gradient selectivity by assessing the ratios C_2/C_4 or C_3/C_4 showed that it is possible to track the changes in the relative extent of most important cracking reactions (monomolecular cracking via pentacoordinated carbonium ions as the initiation step, and bimolecular hydride transfer plus "classical" β-scission of carbenium ions, as propagation steps), since these ratios also represent a relationship between the reactions. As conversion increases for a given catalyst, the magnitude of monomolecular cracking, and consequently the index, decrease until a stable relationship with bimolecular cracking is reached. The apparent energy of activation of monomolecular cracking is higher. Both the changes in zeolite framework electric charge density induced by dealumination and the procedure used for dealuminating the catalysts, which generates different degrees of heterogeneity, influence the relationship between cracking routes. When dealumination is higher, the effect of energy gradients, the protolytic cracking, and consequently, the index, increase; this approach also shows that steam dealumination produces more heterogeneous zeolite aluminum distributions than equilibration in commercial FCC units. © 1998 Academic Press

INTRODUCTION

The complex mechanisms of hydrocarbon cracking reactions on acidic catalysts, specially zeolites, have been extensively studied, mainly through the conversion of small paraffin molecules (1). In order to account for the observed product distributions, two routes were considered: the protolytic cracking via a pentacoordinated carbonium ion, and the classical carbenium ion, β-scission reactions. These two paths were considered either independently (2–5) or, more recently following an integrating concept, as taking part of a whole, single "chain mechanism," including initiation, propagation, and termination reactions (1, 6). Under this approach, monomolecular reactions (cracking of a carbonium ion formed by protonation of a feed molecule, yielding a paraffin molecule and a carbenium ion) and bimolecular reactions (interaction between a carbenium ion accepting a hydride ion from a feed molecule and further β-scission of the newly originated carbenium ion) are distinguished.

In order to account for the relative incidence of these cracking reactions, a number of indexes were developed. Wielers *et al.* (5) defined the "cracking mechanism ratio" in the conversion of *n*-hexane as the rate between the selectivities for methane plus ethane and ethylene, indicative of protolytic cracking, and iso-butane, indicative of β-cracking. Corma *et al.* (6) cracked isobutane and described the incidence of monomolecular reactions by means of the initial selectivities for methane plus hydrogen while bimolecular reactions would be expressed by the selectivities for the rest of the products. Shertukde *et al.* (7) referred to the ratio between bimolecular and monomolecular processes as "chain length" by relating the consumption of feed molecules through hydride transfer reactions and protonation, respectively. Later, the "kinetic chain length" was defined by Zhao *et al.* (8) as the ratio between the total rate of feed conversion and the initiation reactions by protolysis.

Following different concepts and objectives, another particular index was defined by Mirodatos and Barthomeuf (9), who observed that in the cracking of various paraffin reactants over different zeolites, the ratios between the compounds with two (C_2), or three (C_3), carbon atoms per molecule, and compounds with four carbon atoms per molecule (C_4), were representative of what they defined as "energy gradient selectivity" in zeolites. The concept points to changes in the distributions of products due to electric field effects in the small pores of zeolites. It was initially applied to the cracking of relatively low molecular weight paraffins over pure zeolites (9, 10), but the index showed a striking regularity when assessed under the micro activity test (MAT) philosophy in the cracking of a vacuum gas oil with many dealuminated catalysts used in the process of catalytic cracking of hydrocarbons (FCC) (11). Although the index is system-specific (it depends on reactant, catalyst type, and experimental conditions), it looks like a useful tool to identify zeolite properties, as long as more details

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[1] Corresponding author. E-mail: usedran@fiqus.unl.edu.ar.

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about the influence of the parameters that control its behavior are known.

It is the objective of this work to contribute to the elucidation of the relative incidence of most important steps in the catalytic cracking of paraffin hydrocarbons on different Y zeolite FCC catalysts, as a function of various parameters (temperature, conversion, and catalyst dealumination covering a wide range of compositions). The significance of the C_2/C_4 (or similarly, C_3/C_4) ratio to characterize the catalytic performance of Y zeolites dealuminated by different methods, so as to obtain various degrees of heterogeneity in the charge distributions, was considered in that sense. Singular tools, like a fluidized bed discontinuous laboratory reactor, very short contact times, compound commercial FCC catalysts, and a relatively high molecular weight reactant, under a wide range of conversions, were used.

EXPERIMENTAL

The catalysts used were Y zeolite-containing, commercial FCC catalysts: catalyst A (Octydine 1160BR, Engelhard); catalyst B (HFZ33, Houdry); catalyst E-CAT-E (PRE-50AR, Engelhard), and catalyst E-CAT-O (Octavision 519, FCC S.A.). Catalysts E-CAT-E and E-CAT-O, with inactive matrix, were equilibrium samples obtained from running FCC units. When dealuminated in the laboratory, fresh catalyst samples were treated in a fluidized bed reactor with 100% steam for different times at 815°C. Zeolite unit cell sizes (UCS) were assessed by means of the ASTM technique D-3942-85, using a Shimadzu XD-1 X-ray spectrometer. Specific surface area (zeolite and matrix) were determined by means of conventional nitrogen adsorption isotherms (12). The resulting properties of the catalysts are summarized in Table 1.

The conversion of n-hexadecane (n-C_{16}, Fluka, minimum 99.9%) was conducted in an internal recirculation, fludized bed discontinuous stirred tank reactor with the catalyst kept in a chamber between two metal porous plates that allows the close simulation of conditions in industrial FCC riser units (13). When the target temperature and mixing conditions were achieved, a given amount of reactant was injected and timers were activated simultaneously; after the reaction time was attained, the reactor was automatically opened to a vacuum system that evacuated the products very rapidly and from which a sampling valve could be filled. In this way, very short contact times could be achieved. Experiments were performed with reaction times from 1 s to 60 s, in the range of 440 to 550°C. In most of the experiments, the mass ratio of catalyst to reactant was 5.14. Thermal cracking reactions were performed under similar conditions, with the reactor loaded with inert silica particles. Reaction products were analyzed by gas chromatography.

TABLE 1

Properties of the Catalysts Used

Catalyst	Steaming time (h)	Specific surface area ($m^2\ g^{-1}$)	Zeolite content (wt.-%)	Zeolite UCS (nm)	RE oxide content (wt.-%)
A-1	1	230	17.3	2.441	1.30
A-4	4	212	14.3	2.427	1.30
B-1	1	222	10.9	2.438	1.93
E-CAT-E	Equilibrium	147	11.5	2.429	1.42
E-CAT-O	Equilibrium	151	15.9	2.424	0.00

RESULTS AND DISCUSSION

The concept of "energy gradient selectivity" was developed by Mirodatos and Barthomeuf (9) to explain, distinctly from shape selectivity effects, the influence of local intracrystalline electrostatic potential gradients on the products resulting from the conversion of paraffin hydrocarbons. Experimental data to assess the value of the C_3/C_4 or C_2/C_4 ratio, preferably C_3/C_4, in which no distinction was made between the different hydrocarbon types inside each group, were gathered from the conversion of model n- alkanes (C_7, C_8, C_{10}) on different zeolites (erionite, ZSM-5, offretite, mordenite, Y (9, 10)) and SAPO-37 (14). When faujasite zeolites were studied, the Si/Al ratio was changed only up to 7 (14). According to this concept, they postulated that higher index values would imply higher incidence of protolytic cracking against bimolecular hydride transfer and β-scission cracking, since energy gradient effects would facilitate molecule polarization and bond weakening in the ends, thus favoring the production of shorter chain products. The index was claimed not to depend on acid strength of active sites or conversion (15) but on field (energy) gradient in the pores due to charge spatial distribution.

n-Hexadecane is a paraffin hydrocarbon with a molecular weight which is intermediate between that of lighter paraffins (C_7 to C_{10}) or gas oil feedstocks (11) previously used in connection with the concept of energy gradient selectivity. The conversion of n-C_{16} as a test reactant has proved to be useful for FCC related studies (16–18). Its reaction over commercial FCC catalysts, which comprises a wide distribution of products (refer to examples in Table 2), will be analyzed here mostly in terms of the mass ratios between products with different carbon atom numbers per molecule (preferably C_3/C_4 or C_2/C_4), assuming that activity and selectivity in this type of catalysts is largely controlled by the zeolitic component (19, 20). The evolution of conversion as a function of reaction time for the equilibrium catalysts is shown in Fig. 1 as an example in which it can be seen that E-CAT-E (UCS, 2.429 nm, zeolite content 11.5%) is more active than E-CAT-O (UCS, 2.424 nm, zeolite content 15.9%), since it reaches the same conversion value at a shorter reaction time; as expected for a given catalyst, the higher the temperature, the steeper the slopes of the curves.

TABLE 2

Conversion of *n*-Hexadecane

Products	Reaction temperature 500°C	550°C
C_1	0.037	0.201
$C_2^=$	0.191	0.689
C_2	0.075	0.344
$C_3^=$	3.054	5.188
C_3	0.906	1.724
i-C_4	3.392	4.166
1-$C_4^=$ + i-$C_4^=$	2.076	3.319
n-C_4	1.284	1.870
t-$C_4^=$	1.079	1.607
c-$C_4^=$	0.797	1.203
3Me-1-$C_4^=$	0.106	0.162
i-C_5	3.493	4.008
1-$C_5^=$	0.210	0.430
2Me-1-$C_4^=$	0.515	0.770
n-C_5	0.671	0.908
2Me-1,3-butadiene	0.060	0.067
t-$C_5^=$	0.504	0.720
c-$C_5^=$	0.256	0.412
2Me-2-$C_4^=$	1.089	1.507
$C_6^=$	1.478	2.101
C_6 paraffins	3.093	3.248
C_7	1.872	2.154
C_8	2.159	3.034
C_9	0.097	0.146
$C_{10\text{-}12}$	0.436	0.894
$C_{13\text{-}15}$	1.157	0.818
C_{16}	69.915	58.310

Note. Example product distributions at 500 and 550°C over catalyst E-CAT-O. Reaction time, 9s.

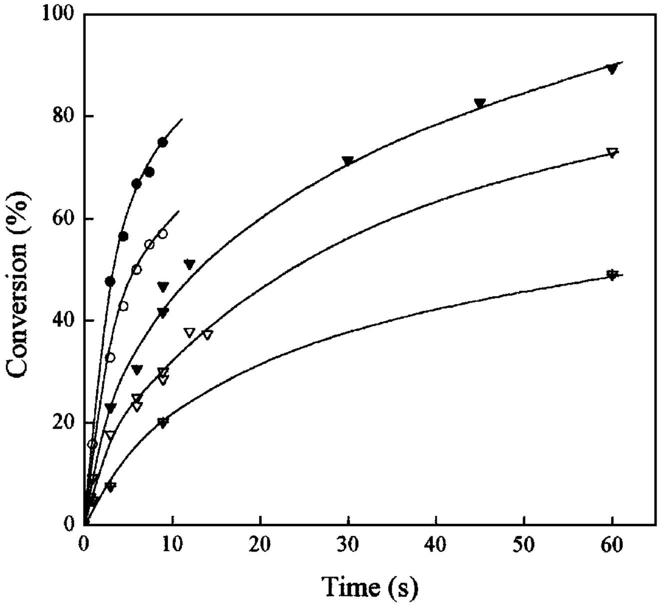

FIG. 1. Conversion as a function of reaction time. Symbols: ●, E-CAT-E, 550°C; ○, E-CAT-E, 500°C; ▼, E-CAT-O, 550°C; ▽, E-CAT-O, 500°C; ∀, E-CAT-O, 440°C.

The values of the ratio C_2/C_4 for catalyst E-CAT-O as a function of reactant conversion at the various temperatures used are shown in Figs. 2a to 2c. It can be seen that in all cases the ratio follows the same qualitative behavior, decreasing when conversion attains values of about 20% and then keeps stable ("steady") values. This decrease in the index as conversion increases is progressively faster with increasing temperature, and the higher the temperature, the higher the "steady" values, which are 0.017, 0.030, and 0.120 at 440, 500, and 550°C, respectively. It can be seen in Fig. 2b that the same profile is also shown by catalyst E-CAT-E, going to a "steady" value of 0.020. It is as well apparent in Figs. 2b and 2c that the value of the index depends on the properties of the catalyst (e.g., the values in Fig. 2b, (500°C) for the catalysts A-1, B-1, and E-CAT-E are 0.041, 0.048, and 0.030, respectively), a fact that will be discussed later. It has to be noted that for a given catalyst and conditions, the "steady" indexes have standard deviations lower than 0.008. The same qualitative behavior was observed for the ratio C_3/C_4, which is included in Fig. 2a as an example. Some other possible ratios, like C_2/C_5, C_3/C_5, C_2/C_6, or C_3/C_6, besides having evolutions that are coincident with those shown in Figs. 2a to 2c, at low and intermediate conversions, increase when conversion is higher, a fact that could be assigned to the beginning of an overcracking regime consuming C_6 or C_5 molecules more significantly.

The contribution from thermal cracking reactions could be considered relatively high when the conversion is low (short contact times), since they would yield selectively higher amounts of light products, thus influencing the evaluation of the index C_2/C_4. However, experiments with inert particles in the reactor showed that purely thermal conversions are much lower than those obtained with catalysts under the same temperature and reaction times (refer to Table 3). Product distributions, as well, are clearly different, since the yield of ethylene is very significant. Moreover, it has to be noted that besides the fact that at 440°C the thermal conversion is very small, the evolution of the index is still the same (see Fig. 2a). Then, the variations in the C_2/C_4 values in the low conversion ranges (refer to Figs. 2a to 2c) can be considered a consequence of the catalyst performance.

TABLE 3

Thermal and Catalytic Conversions under the same Experimental Conditions; catalyst E-CAT-O

	Conversion (%)					
	T = 440°C		T = 500°C		T = 550°C	
Reaction time (s)	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
1	nil	4.8	1.0	9.1	n.a.	8.5
3	nil	7.5	n.a.	17.7	6.0	17.0
9	0.7	20.1	2.4	28.6	16.9	46.8

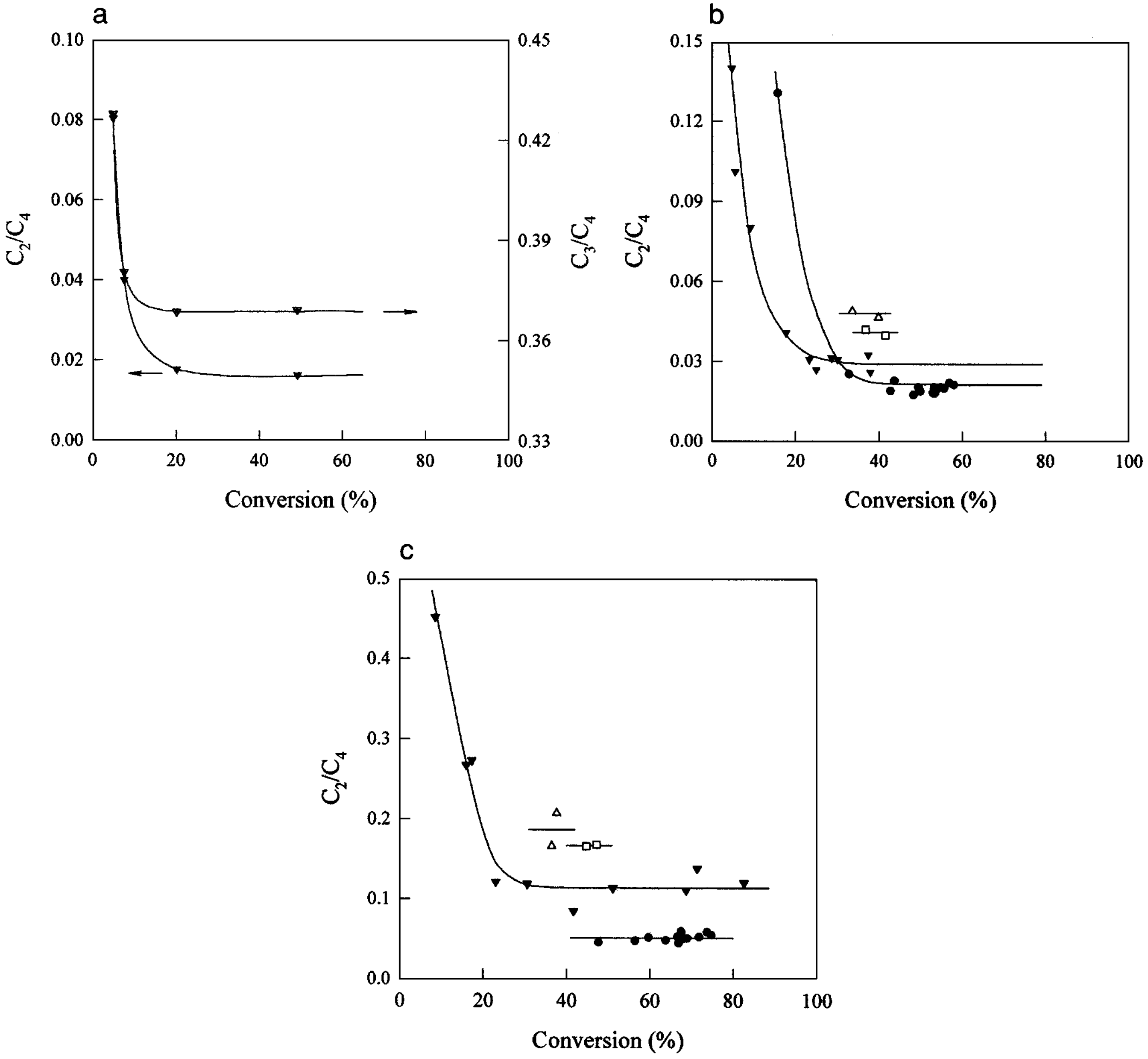

FIG. 2. C_2/C_4 ratio as a function of conversion: (a) *T*: 440°C (C_3/C_4 ratio is also included); (b) *T*: 500°C; (c) *T*: 550°C. Symbols: □, A-1; △, B-1; ●, E-CAT-E; ▼, ▽, E-CAT-O.

It could be accepted that the ratios C_2/C_4, or C_3/C_4 indicate a relationship between the two cracking processes that participate in a "chain mechanism"; for given reaction temperature and catalyst properties, when conversions are low, the monomolecular cracking process via pentacoordinated carbonium ions has a more significant presence, or it could even be considered the initiation step (3); at higher conversions, the bimolecular "classical" β-scission cracking process via carbenium ions, prevails more neatly. In other words, this index represents a comparison between pentacoordinated carbonium ion- and "classical" carbenium ion-conducted reaction paths. On a certain catalyst, the pentacoordinated carbocation route is by far the major source of shorter hydrocarbons (indeed, the formation of carbonium ions of different size is similar from the energetic standpoint (21)), while the formation of smaller size products (say, C_2 or C_3 in this case) from "classical" carbenium ion cracking, is not favored (22). These two processes have also been referred to as pointing to the existence of two different cracking reaction mechanisms (2, 5, 10). Then, the results presented in Figs. 2a to 2c are fully consistent with this scheme and previous works (1, 2), and the indexes reveal

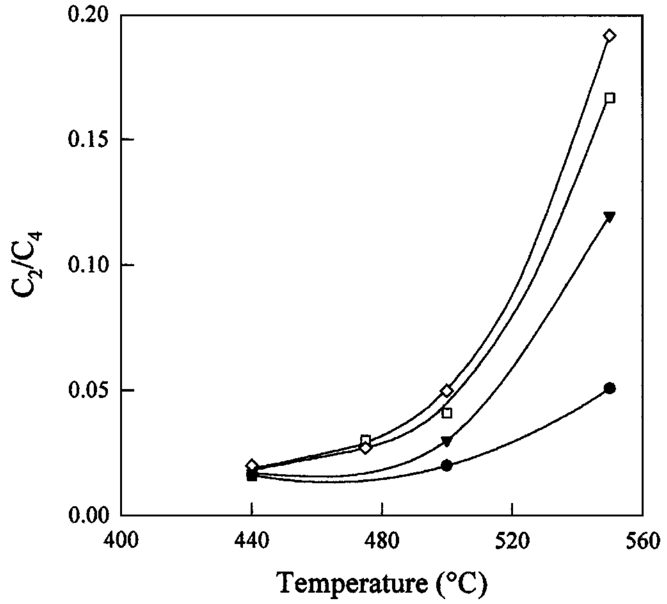

FIG. 3. C_2/C_4 ratio as a function of temperature. Symbols as in Fig. 2; ◇, A-4.

the interplay between cracking processes, their magnitudes changing as a function of conversion as expected. It is to be noted that the fact that the curve for catalyst E-CAT-E is above the one for E-CAT-O at low conversions, and the opposite is true at high conversions (refer to Fig. 2b), is consistent with the properties of the catalysts. In effect, if site densities are compared, it can be seen that E-CAT-E has a higher site density. Then, accepting that the acid strengths are comparable, E-CAT-E reaches the same conversion as E-CAT-O at a much shorter reaction time (see Fig. 1) due to its higher site density, and the index would still be changing its value since the reaction would still be in the initiation steps, while E-CAT-O has already reached its "steady" condition. It can be seen that the conversion value needed to get the "steady" condition on each catalyst is reached at approximately the same contact time.

The values of the C_2/C_4 ratio as a function of reaction temperature on different catalyst samples are shown in Fig. 3. Data were obtained from the regions of "steady" behaviors, since at that conversion range, the index values reflect that a full relationship between reactions (monomolecular protolytic cracking and bimolecular β-scission cracking) had developed, which shows that an equilibrium had been reached. Note that at lower conversions the relation between reactions is very dynamic and changes continuously (refer to Figs. 2a and 2b). It can be seen that the effect of increasing reaction temperature was to increase the values of the index, thus suggesting that the apparent energy of activation for the process of monomolecular cracking via carbonium ions is higher than that of classical β-scission of carbenium ions. This is consistent with previous observations on the conversion of smaller molecular weight reactants (2, 5, 23). As mentioned before, this would be a purely catalytic effect. Again we stress that the same qualitative behavior was observed for different ratios (e.g. C_2/C_5, C_3/C_5, C_2/C_6 or C_3/C_6). The values of the index in Fig. 3 show that, in general, they increase faster as a function of temperature on catalysts that were steam dealuminated in the laboratory as compared to equilibrium samples.

As described above, the model on which the definition for the C_2/C_4 index is based points to the existence of electric field gradients inside the pores in the zeolite framework, with different magnitudes according to catalyst properties, particularly the density of electric charges, i.e. the concentration of aluminum atoms (9, 10). Then, the process of dealumination in Y zeolites, subsequently leading to variations in charge density and electric field gradients (24, 25) should mirror as changing values in the index when catalysts of the same type (e.g., zeolite Y) with different extent of dealumination are employed. These differences in charge distributions also induce different states concerning the homogeneity of catalyst properties (14). Concerning FCC catalysts, the zeolite dealumination and associated strong variations in the properties of the catalyst when it is modified from its fresh state to the equilibrium one, are the consequences of the severe environments that the catalyst particles face in the cyclic operation between regenerator and riser reactors. Then, it is interesting to observe the changes in the index values as a function of dealumination. Figure 4 shows them

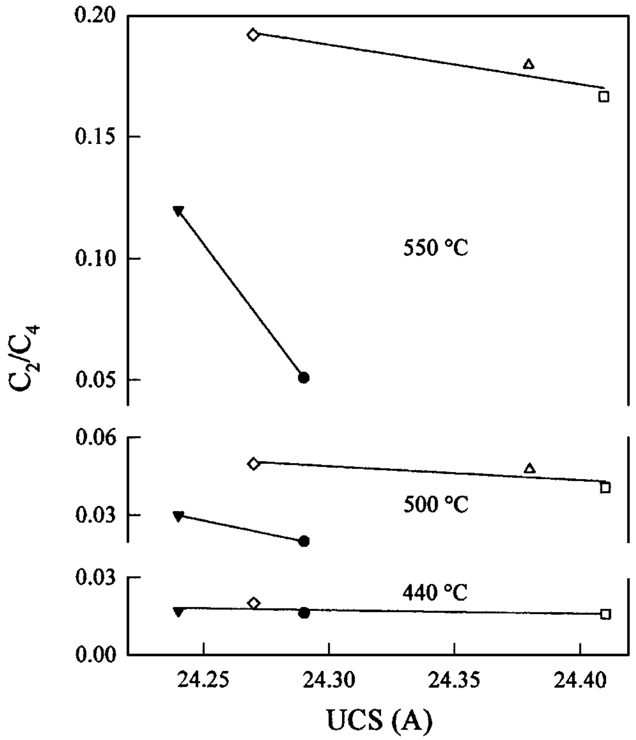

FIG. 4. C_2/C_4 ratio as a function of zeolite unit cell size. Symbols as in Fig. 3; open: steam dealuminated catalysts; closed: equilibrium catalysts.

as a function of unit cell size, which is an equivalent expression of Y zeolite aluminum content, in the range of 2.424 to 2.441 nm; these unit cell sizes imply that the Si/Al ratios change in the range of about 7 (Catalyst A-1) to about 30 (Catalyst E-CAT-O) (20), which is far in excess of previous research on this type of catalysts (14). It is to be noted that statistical analysis allows to state that the observed trends are outside the experimental uncertainty. It can be seen that in general, the smaller the unit cell sizes, the higher the index. As discussed above, this would also imply a higher incidence of monomolecular cracking reactions. The increase of the index at lower UCS could be rationalized in terms of higher localized disturbing influences of field gradients on reacting molecules, owing to increasing site isolation. In this way, polarization and weakening of the C-C bonds in the extremes of the molecules occur, which facilitates protonations and monomolecular cracking, thus increasing the production of smaller fragments (14, 15).

However, it is clear that charge density as expressed by aluminum atom density is not the only parameter to be considered. In effect, for a certain zeolite aluminum content (same unit cell size), the index values are different, depending on the nature of the dealumination process; this is more evident at the highest reaction temperature of 550°C. It has been shown that steam-dealuminated FCC catalysts exhibit more heterogeneous aluminum distributions in the zeolite crystals if compared against equilibrium catalysts (26). A more heterogeneous distribution of charges is expected to induce more intense field gradients, which, in terms of cracking processes, would translate into a higher incidence of pentacoordinated carbonium ion cracking, i.e. an increase in the C_2/C_4 index (refer to the previous paragraph). Then, the higher index values that are observed in our steam dealuminated samples in comparison to equilibrium catalysts at the same temperature and aluminum content could be due to this fact. It can be also observed in Fig. 4 that the rate of change of the index as a function of dealumination is different, depending on the dealumination treatment. According to the previous description about the homogeneity of the aluminum distributions corresponding to each treatment, the higher heterogeneity in steam dealuminated catalysts would overimpose and somewhat mask the effect of charge density. On the contrary, in equilibrium samples, with more homogeneously distributed charges, the effect of charge density is more pronounced.

CONCLUSIONS

Energy gradient selectivity in zeolites, as assessed by means of different relationships between hydrocarbon groups (preferably C_2/C_4 or C_3/C_4), was confirmed on commercial, Y zeolite FCC catalysts when cracking *n*-hexadecane at various temperatures. These relations constitute a useful tool to characterize the catalytic properties of dealuminated Y zeolites. On a given catalyst, experiments at very short contact times showed that the index certainly changes as a function of conversion and describes the relative importance of the cracking reactions (monomolecular, pentacoordinated carbonium ion cracking and bimolecular, hydride transfer plus β-scission carbenium ion cracking). The importance of monomolecular cracking, which is the initiation process, decreases as conversion increases, to reach a "steady" relationship with bimolecular cracking. The energy of activation of the initiation step is higher than that of bimolecular cracking.

Concerning specifically the concept of energy gradient selectivity, it also shows that the energy gradients and reactions' prevalence are influenced by catalyst composition through both charge density (in turn a consequence of dealumination) and heterogeneity resulting from the procedure used (steaming, leading to more heterogeneous distributions, or equilibration in commercial units). They were both changed widely in this study. In this way, different energy gradients result for the same aluminum content, which impact on the ratio between reactions. Then, it has been shown that this fundamental concept can be applied with certainty to complex commercial catalysts.

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