

Formation of Products Responsible for Motor and Research Octane of Gasolines Produced by Cracking

The Implication of Framework Si/Al Ratio and Operation Variables

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An alkane in the range of gasoline fraction (*n*-heptane) has been used as a reactant to study the influence of zeolite Y catalyst and process variables (i.e., framework Si/Al ratio and procedure of dealumination, time on stream, and contact time) on the formation of products responsible for motor and research octane of gasoline during cracking, namely branched, aromatics, and olefins. It is found that the branched isomers in the C₅ and C₆ fractions appear as primary products and are partly produced by disproportionation, since the ratio of iso to normal compounds is above equilibrium. The ratio of branched to linear products strongly decreases when the number of carbon atoms of the product fraction increases. It goes through a maximum for samples with unit cell size in the range 24.30–24.40 Å. The selectivity to aromatics is strongly dependent on total conversion and increases with time on stream, while dealumination decreases the selectivity to aromatics. The saturation of olefins, via hydrogen transfer, decreases with increasing dealumination, increasing temperature and decreasing time on stream. These observations are explained not only on the basis of site density and strength but also on the basis of the adsorption characteristics of the samples. Finally, methane and ethane can be formed by a protolytic cracking of branched products. Part of these two gases and most of the ethylene are formed by a radical type of cracking, in which extraframework aluminium plays an important role. © 1989 Academic Press, Inc.

INTRODUCTION

Since the early days of catalytic cracking, and until very recently, refiners were mainly concerned with catalysts which maximize the yield of gasoline. The quality of the resultant gasoline, i.e., octane number (ON), was not a critical point since this could be improved by adding tetraethyl lead to the final pool. However, greater environmental restrictions on such additives have forced the refiners to seek other noncontaminant additives (1, 2) while searching for further possibilities of increasing ON in the reforming units. There is no doubt that the FCC is the main gasoline producing unit in a refinery, and any effort directed toward improving the quality of gasoline produced should be worthwhile.

In addition to improvement due to modification in the process operation (3, 4) much hope is placed on improvements in octane by new catalyst formulations. Following this, the catalyst should show, in addition to activity and selectivity to gasolines, a good selectivity for branching isomerization, aromatics, and olefins. Since branched alkanes and alkenes as well as aromatics can further react under the cracking conditions, it appears to us that better knowledge of the reaction patterns, and of the influence of the different active sites, acid strength, and density for catalyzing the consecutive and parallel reactions occurring during catalytic cracking, could be one way to better direct the process versus the formation of the desired products. It is apparent that catalyst optimization for future octane catalysts will imply subtle effects, the determination of which will be based on

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systematic studies of the fundamentals of the cracking and the other accompanying reactions. It is according to this line of thinking that cracking of pure hydrocarbons on well-defined catalysts can improve our basic knowledge of the catalyst factors governing the formation of a given product.

In the present work *n*-heptane has been employed because it is a characteristic molecule of the gasoline fraction which is sufficiently large to allow different modes of cracking, isomerization, cyclization, etc., to take place in the presence of cracking catalysts. The influence of acid site strength, density, and nature on the modes of cracking, branching isomerization, aromatization, and hydrogen transfer has been studied and from the results, the ON behavior of the gasoline fraction can be predicted. The influence of other zeolite characteristics such as dimensionality and pore dimension will be analyzed in a following paper.

EXPERIMENTAL

Materials

The starting NaY zeolite was an SK-40 from Union Carbide with a 2.4 framework Si/Al ratio. Ultrastable HY zeolites were prepared by steaming (HYUS) or by SiCl₄ treatment (HYD). The HYUS samples were prepared by steam calcination at atmospheric pressure and 500–750°C for 3–20 h of partially ammonium-exchanged zeolites. After steaming they were exchanged twice with an NH₄⁺ solution at 80°C for 1 h and then calcined at 550°C for 3 h. In this way dealuminated samples containing less than 2% of the original Na⁺ were obtained.

Samples dealuminated with SiCl₄ were prepared by following the procedure described by Beyer and Belenkaya (5) and working at 250–500°C. Textural and structural characteristics of the zeolite samples are given in Table 1. The unit cell constant of the zeolites was determined by X-ray diffraction using CuK α radiation and following ASTM procedure D-3942-8. The estimated standard deviation was ± 0.01 Å.

The crystallinity of the samples was calculated by comparing the height of the (5,3,3) peak and considering the NaY SK-40 as 100% crystallinity.

Catalytic Experiments

The catalytic experiments were performed in a continuous flow glass tubular reactor at 450°C, atmospheric pressure, and a catalyst-to-oil ratio (cat./oil) in the range 0.017–0.180. The cat./oil is defined as the amount of catalyst divided by the total amount of *n*-heptane fed in a given time on stream (TOS). For a fixed cat./oil the TOS was varied by changing the speed of feeding in a positive displacement pump. The zeolite was pelletized and crushed and the selected particle size was 0.50–0.75 mm for which no control of internal diffusion was observed.

The experimental procedure was as follows: A given amount of *n*-heptane was introduced into the reactor at constant velocity, and the effluent from the reactor passed through a water–ice cooled condenser. When the run was finished the reactor system was stripped by a stream of N₂ at reaction temperature for 10 min, and the gaseous stream was introduced into a gas burette saturated with NaCl. Total reaction products were analyzed by GC.

TABLE 1

Textural and Structural Characteristics of the HYUS and HYD Samples

Zeolite	Si/Al ^a	(Å)	u.c. Si/Al ^b	Al/u.c. ^b	Cryst. (%)
HYUS-1	2.9	24.48	5.9	27.8	85
HYUS-2	2.8	24.42	8.1	21	90
HYUS-3	2.8	24.28	35.3	5.3	75
HYUS-4	—	24.26	63	3	85
HYUS-5	2.3	24.24	141	0.8	70
HYD-1	—	24.50	5.4	30	70
HYD-2	3.4	24.45	6.9	24.4	95
HYD-3	—	24.35	13.8	13.1	80
HYD-4	4.0	24.31	21.2	8.7	90
HYD-5	10.4	24.22	—	—	90

^a From chemical analysis.

^b Calculated from Fichtner–Schmittler equation (19).

Total conversion (\bar{X}) is defined as the total number of carbon atoms of outlet hydrocarbons, other than the feed, divided by the number of carbon atoms in the *n*-heptane fed. The yield of a product is defined as number of moles of product divided by number of moles of *n*-heptane fed, and the product selectivity was calculated by dividing the number of moles of product by the number of moles of *n*-heptane cracked. Only the experiments with mass balance above 95% were considered.

RESULTS AND DISCUSSION

Catalytic cracking is a difficult process to study in detail. Indeed, at the relatively high temperatures at which it takes place the network of the reaction involves a large number of interconnected parallel and consecutive reactions. All this, together with the fact that the catalyst activity decays very fast, makes differentiation difficult between activity and selectivity effects (due to changes in reactor or operation variable: conversion level, TOS, temperature, etc.) with those effects due to the physicochemical characteristics of the zeolite catalysts. Moreover, sometimes authors discuss the influence of the zeolite structure on the cracking behavior in terms of different framework Si/Al ratios. Since it is well known that some zeolites can be synthesized only with high Si/Al ratio, it is obvious that unless special care is taken in keeping all parameters but one constant, the results can be confusing due to the overlapping of structural and compositional factors. Here we have tried to separate the different compositional and structural variables by taking into account the influence of TOS and \bar{X} on product distribution, and then looking first to the influence of the Si/Al ratio using zeolite Y in a very wide range of framework aluminum content (30–1 Al/u.c.), obtained by different procedures of dealumination. After this we will be in a good situation to look into the structural effects.

Selectivity Results in n-Heptane Cracking

In Figs. 1 to 8 we have plotted the behavior of the paraffin-to-olefin (P/O), *i*-C₄-to-total C₄ (*i*-C₄/*t*-C₄), *i*-C₅-to-*n*-C₅, 2 + 3-methylpentane-to-*n*-hexane (2 + 3MP/H), 2-to-3-methylhexane, C₂-to-C₅, and C₃-to-C₄ ratios and aromatic fraction versus \bar{X} , TOS, and framework Si/Al ratio in the cracking of *n*-heptane at 450°C.

The P/O ratio in the products is a measure of the hydrogen transfer ability of the zeolite catalyst. On the other hand hydrogen transfer is a consecutive reaction which produces the saturation of olefins formed in a primary cracking. Then it is not surprising that independently of the framework Si/Al ratio of the zeolite the P/O ratio increases with the conversion (Fig. 1a). These results show that in order to evaluate the hydrogen transfer ability of two catalysts the results should be compared at the same level of conversion or even better by means of the yield curves versus total conversion (\bar{X}). It is not uncommon to find in the literature catalyst comparisons made in ranges in which "similar conversions" are considered, for instance, in the range 5–10%. However, from Fig. 1a it is apparent that the P/O ratio changes $\approx 40\%$ in even that "small" range of conversion (5 to 10%). Therefore if the variation of P/O ratio with conversion is not strictly considered, the conclusions obtained when comparing the behavior of different zeolites can be quite misleading. The TOS, in the range studied here (Fig. 1b), has little influence on the final P/O ratio. A very slight increase in that ratio is observed when the TOS is increased.

In Fig. 1c the influence of the framework Si/Al ratio of Y zeolites at 5% level of total conversion and 150 s of TOS is shown. The P/O ratio, and consequently the hydrogen transfer, decreases when the Si/Al ratio increases. This might be a consequence of the lower (total) density of acid sites in dealuminated zeolites or of the predominance of very strong acid centers wherein

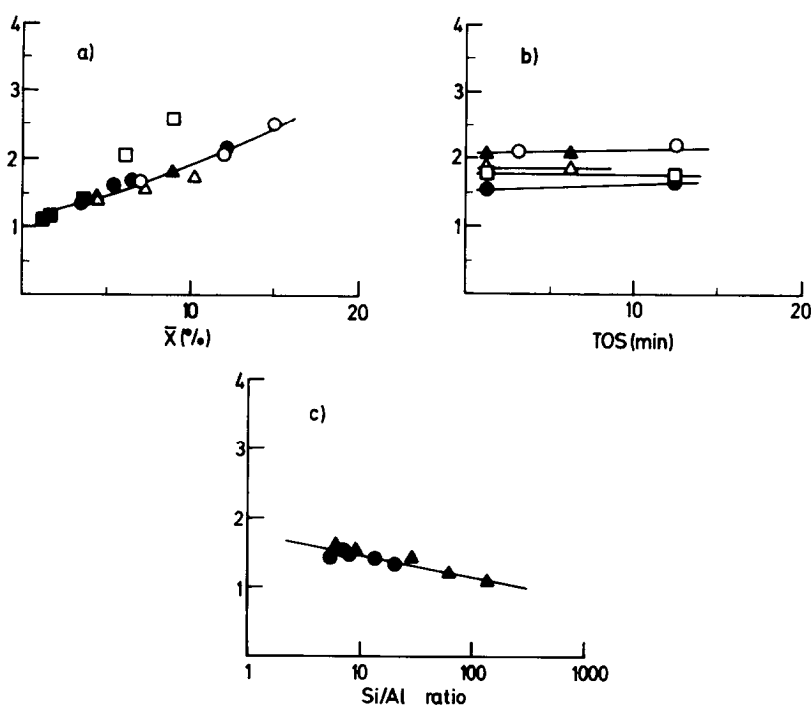


FIG. 1. Paraffin/olefin ratio in HYUS and HYD zeolites. (a) Influence of conversion at TOS = 150 s; (○) HYD-2, (△) HYD-3, (□) HYD-4, (●) HYUS-1, (▲) HYUS-2, (■) HYUS-3. (b) Influence of TOS at $X = 10$ – 13% ; (○) HYD-1, (△) HYD-2, (□) HYD-3, (●) HYD-4, (▲) HYUS-2. (c) Influence of Si/Al ratio at $X = 5\%$ and TOS = 150 s; (●) HYD, (▲) HYUS.

the intrinsic rate of the cracking/hydrogen transfer ratio is higher than that in the less strong acid centers more abundant in zeolites with a higher aluminum content. It is not always possible to separate the effects of these two phenomena since both variables change in parallel. Nevertheless the results of Pine *et al.* (6) show that in gas-oil cracking over HYUS zeolite catalyst, small amounts of sodium strongly increase the hydrogen transfer and consequently decrease the research octane number (RON) of the gasoline obtained. One should expect that the Na^+ ions would preferentially eliminate the strongest, i.e., the more isolated, acid sites decreasing the acid strength of the remaining acid sites. If this is so it is apparent to us that hydrogen transfer is influenced not only by the site density but also by the strength of acid sites. There is however one aspect which cannot be explained by either of the two hypotheses

named above. This is the still decreasing P/O ratio observed (Fig. 1c) for framework Si/Al ratios higher than 20. In these zeolites all Al can be considered isolated, and the average number of Al per supercavity should not be higher than two. It is then difficult that in these circumstances, a further dealumination could influence the hydrogen transfer ability if only strength and density of Brønsted sites would be responsible for the observed P/O ratio. There is a third possibility that will be discussed later and which involves a radical cracking mechanism as an important route in very highly dealuminated zeolites.

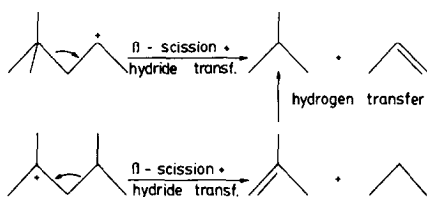
Finally, we must take into account that by increasing the framework Si/Al ratio, the adsorption properties of the zeolite will be affected; i.e., the adsorption will decrease when the Si/Al ratio increases. This will have a negative effect on the rate of bimolecular reactions such as hydrogen

transfer. Thus, we can explain the change in the P/O ratio without having to assume that the reaction needs adjacent acid sites as it is assumed by the models reported in the literature. Indeed it has been reported (6, 7) that the dealumination increases the distance between sites, and when the distance increases the hydrogen transfer decreases. If this is so, it becomes, on the other hand, difficult to accept a model which involves bimolecular reactions following a Langmuir–Hinshelwood mechanism since then two positively charged adsorbed molecules will have to be interacting at short distances.

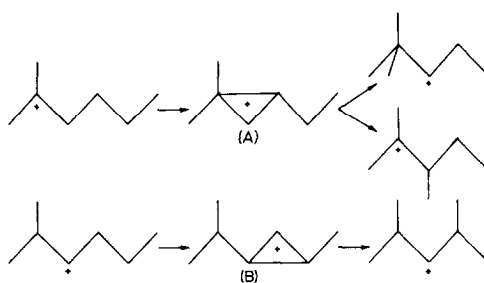
The observed $i\text{-C}_4/t\text{-C}_4$ ratio is influenced by the dimension of zeolite cavities. Indeed, as has been reported before (8, 9) the i -butane will be formed mainly by cracking of the 2,2'-dimethylpentane and also by hydrogen transfer of the i -butene which comes from the cracking of the 2,4-dimethylpentane according to Scheme 1.

If we take into account that the dibranched carbenium ions are obtained by rearranging the monobranched ones via PCP (protonated cyclopropane rings) intermediates (10, 11), the PCP mechanism giving the dibranched isomers will be as shown in Scheme 2.

Intermediate A is responsible for the formation of 2,2'-dimethylpentane, which in turn gives i -butane by cracking. Intermediate B is responsible for the formation of 2,4-dimethylpentane which gives i -butene by cracking. Intermediate A is slightly bulkier than intermediate B, and both are certainly bulkier than any of the PCP intermediates giving the monomethyl-branched isomers. If this is so, then zeolites with small cavities



SCHEME 1



SCHEME 2

will constrain the formation of 2,2'- and 2,4-dimethylpentane and consequently the formation of i -butane by cracking.

Zeolite Y, with cavities of $\approx 12 \text{ \AA}$, does not restrict the formation of any of the above PCP intermediates, even when contracted because of the severe dealumination. Indeed, in Fig. 2c it can be seen that the $i\text{-C}_4/t\text{-C}_4$ ratio at constant conversion practically does not change with the framework ratio. The TOS does not have a marked influence on that ratio, and an increase in the $i\text{-C}_4/t\text{-C}_4$ ratio is observed when increasing total conversion, probably as a consequence of the transformation of i -butene to i -butane by hydrogen transfer (Figs. 2a and 2b).

The branched isomers of the C_5 and C_6 fractions are observed as primary products and are probably in part produced by disproportionation since the observed ratio is above the equilibrium. Indeed, it would be difficult to explain the high branched-to-unbranched ratio observed only by a β -scission cracking mechanism which would involve primary carbenium ions. It would be possible, however, to obtain $i\text{-C}_5/n\text{-C}_5$ ratios higher than equilibrium, if C_5 are formed predominantly by protolytic cracking of branched heptanes (8), for instance, by the protolytic cracking of 2,3-dimethylpentane (Scheme 3).

At this point it is worthwhile to gain some insight into the carbonium ion chemistry of the C_5 , C_6 , and C_7 hydrocarbons, which are present in high proportions in the gasoline fractions during cracking of gas-oil.

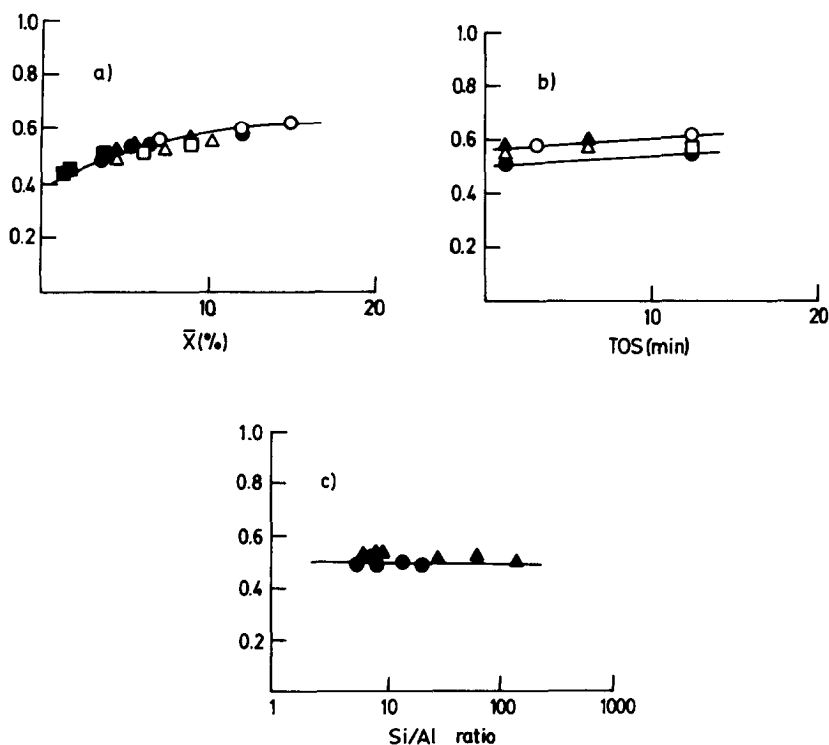
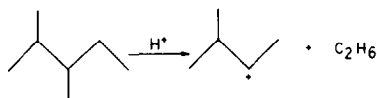


FIG. 2. $i\text{-C}_4/t\text{-C}_4$ ratio in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1.

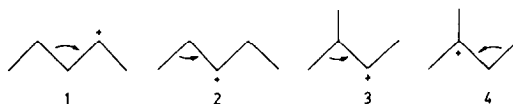
First and in order to predict what could be expected in the C_5 fraction during the cracking process, we have considered the secondary and tertiary carbocations formed in the C_5 fraction (structures 1–4 in Scheme 4). We have not considered the primary ions because they contribute very little to the final products in the cracking reaction due to their very low concentration.

Since any β scission of the above ions go through primary ions, the cracking of structures 1 to 4 will be difficult at moderate temperatures. For instance, the β cracking of molecule 1, which should be the easiest to

crack, involves an activation energy of about $50 \text{ kcal} \cdot \text{mol}^{-1}$ (12). If we take into account that activation energy for the branching rearrangement is of the order of $17\text{--}18 \text{ kcal} \cdot \text{mol}^{-1}$ (12), one would expect that at moderate temperatures the rate of isomerization would be faster than the cracking rate of pentane isomers. Nevertheless, it should be taken into account that the stronger the acid sites responsible for carbenium ion formation the more stable will be primary carbenium ions, and then it could be possible to crack the pentane isomers; even the extension of the cracking



SCHEME 3



SCHEME 4

would not be very big. If we take into account that the $i\text{-C}_5/n\text{-C}_5$ ratios observed are above those of the thermodynamic equilibrium, it appears that most of the $i\text{-C}_5$ should not come from isomerization of $n\text{-C}_5$, but from cracking of highly branched molecules of more than five carbon atoms or, what it is most likely, by condensation–re-cracking (disproportionation) reactions. If this is so and taking into account that disproportionations are bimolecular reactions it appears that if an increase in the ratio of the branched to linear pentanes is desired very high reaction temperatures and very strong acid sites should be avoided.

In zeolite Y when the framework Si/Al ratio increases, the $i\text{-C}_5/n\text{-C}_5$ ratio at 5% total conversion level of n -heptane and 150 s of TOS seems to go through a maximum at Si/Al between 5 and 10 (Fig. 3c). This result may be an indication that the acid sites responsible for disproportionation and

branching isomerization, which are the reactions giving $i\text{-C}_5$, are not the same in strength as those responsible for cracking. Indeed, it is well known (13, 14) that by increasing the framework Si/Al ratio, the proportion of acid sites of medium and weak acidity decreases, and the proportion of the strongest acid sites increases. It has been shown (6, 15) that cracking of short-chain paraffins is catalyzed by the strongest sites, i.e., those with zero aluminums in the second coordination sphere. Taking into account that the maximum in the $i\text{-C}_5/n\text{-C}_5$ is located at a 5–10 Si/Al ratio, we would be inclined to conclude that disproportionation and branching isomerization require weaker acid sites than cracking, probably acid sites with one aluminum in the second coordination sphere. Therefore, in order to obtain a higher ratio of branched isomers to n -alkane in the cracked products it seems that it is not convenient to have very strong

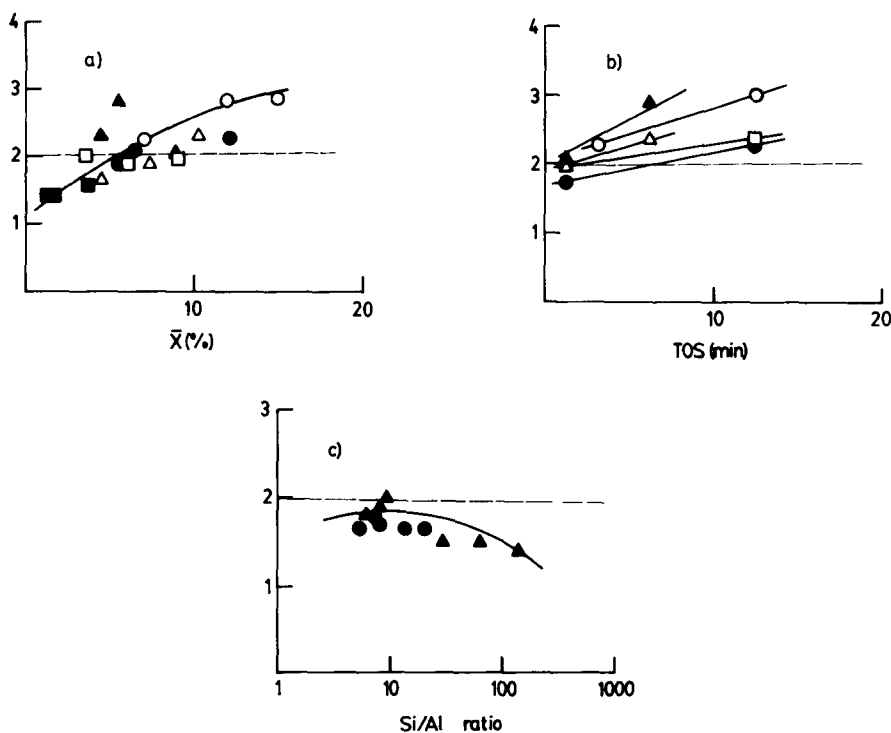
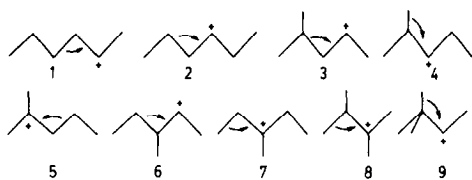


FIG. 3. $i\text{-C}_5/n\text{-C}_5$ ratio in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1; (---) thermodynamic equilibrium.



SCHEME 5

acid sites, but an adequate balance of sites of strong and medium acidity. This conclusion is consistent with the observed effect (Fig. 3b) of the increase in TOS at a constant level of total conversion on the *i*-C₅/*n*-C₅ value. This is due probably to the faster poisoning of the stronger acid sites which may change the distribution of the acid sites when the TOS increases.

In the case of the C₆ fraction the secondary and tertiary ions possibly formed are shown in Scheme 5.

The β scission of structures 1, 2, 5, and 6

involve activation energies of ≈ 50 kcal \cdot mol⁻¹. Isomers 4, 7, 8, and 9 (which generate CH₃⁺ ions) require ≈ 95 kcal \cdot mol⁻¹, while isomer 3, which generates a *sec*-propyl ion and propene involves "only" 31 kcal \cdot mol⁻¹ (12). The β -scission mechanism shown in Scheme 5 indicates that at moderate reaction temperatures, isomerization will also prevail over cracking in the C₆ fraction, but to a lower extent than that in the C₅ fraction. Furthermore, one should consider that structure 3 and the neutral structures 4, 5, 6, 7, and 8 can crack protolytically with activation energies lower than 31 kcal \cdot mol⁻¹, and even structure 9 could crack by protolytic cracking giving CH₄ and *tert*-pentyl carbenium ion with an activation energy sensibly lower than 95 kcal \cdot mol⁻¹. Of course, in the C₆ fraction, cracking of the branched species will increase when the proportion of the stronger acid sites increases (Fig. 4c). Finally, Fig. 4b in-

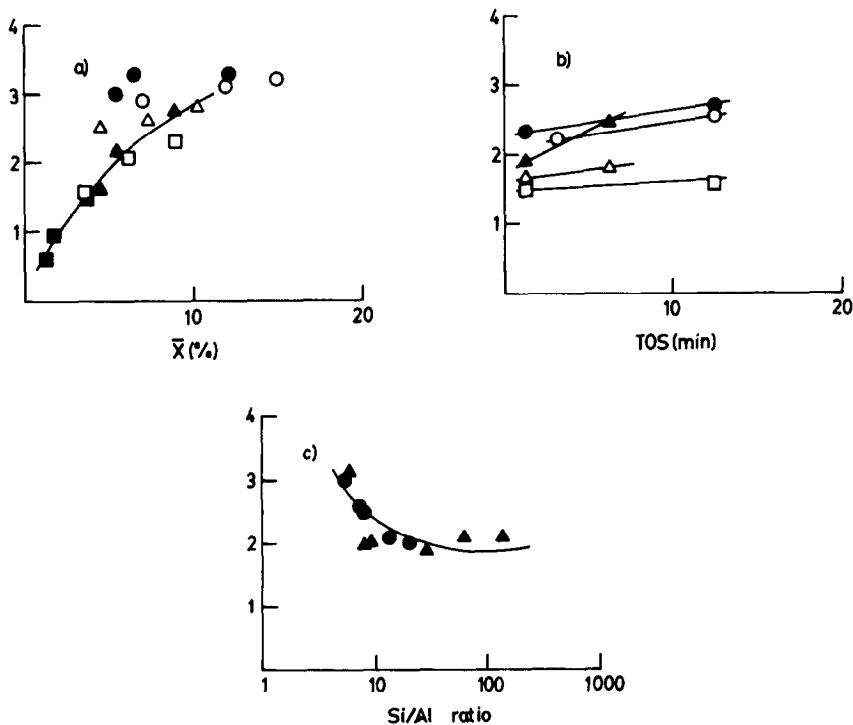


FIG. 4. The 2 + 3-methylpentane to *n*-hexane ratio in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1.

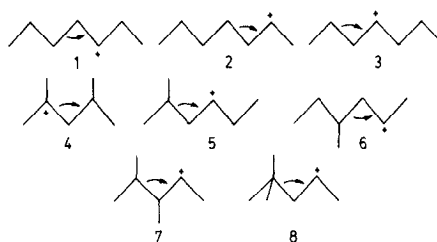
dicates the faster poisoning of the strongest acid sites, i.e., those producing cracking, over the weak and medium acid sites, i.e., those producing isomerization.

At this point we start to see how the longer the hydrocarbon chain in the gasoline fraction the lower will be the branched-to-linear isomer ratio observed in the products. And also, for a given hydrocarbon chain the higher the strength of the sites the lower will be the branched-to-linear ratio of the isomers.

All this becomes especially clear when the monobranched and dibranched C_7 fraction is also introduced (Scheme 6).

In structures 1–8 of Scheme 6 we have not considered the possibilities which give a methyl carbenium ion. Then the β scission of ions 1, 2, and 3 involve ≈ 50 kcal \cdot mol $^{-1}$; 4, 5, 6, 7, and 8 involve ≈ 38 , 34, 30, 26, and 17 kcal \cdot mol $^{-1}$, respectively (8). These results show that in the case of the C_7 fraction the branched-to-unbranched isomer ratio should be smaller than that for C_6 and C_5 , and moreover the main isomer found when a gas-oil is cracked should be 2- and 3-methylhexane since any dibranched isomer can transform via methyl shift to another structure more easily susceptible to cracking.

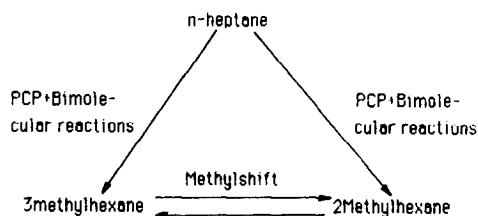
The 2- to 3-methylhexane ratio (2MH/3MH) can be used as one indication of the relative rate of the PCP and the methyl-shift isomerization (10, 16). The predicted value of this ratio via PCP mechanism is 0.5 (10). Therefore if the 2MH/3MH ratio is lower than one corresponding to thermodynamic equilibrium composition and greater than 0.5, the higher the 2MH/3MH ratio the higher will be the rate of methyl shift with respect to the rate of PCP. However, in Fig. 5c the 2MH/3MH ratio obtained is above the equilibrium. This behavior can be explained by considering an isomerization mechanism different from the PCP and alkyl shift, perhaps as indicated by Fajula (17), a mechanism based on bimolecular reactions. On the other hand the 2MH/3MH ratio decreases, progressively approaching



SCHEME 6

the thermodynamic equilibrium, when the framework Si/Al ratio increases. From the above, the influence of the Si/Al ratio in the relative rate of PCP to methyl-shift reactions is not very clear. It can favor either the methyl shift from 2- to 3-methylhexane reaction or the PCP mechanism which would give lower values for the 2MH/3MH ratio (0.5). With respect to these reactions, the TOS has little effect (Fig. 5b) and when the level of conversion increases, the 2MH/3MH ratio approaches the equilibrium (Fig. 5a) in agreement with the reaction scheme in Scheme 7.

The C_2/C_5 and C_3/C_4 ratios can be used as a measure of the importance of disproportionation and re cracking of the primarily formed products with respect to normal direct cracking of the C_7 molecules. In Figs. 6 and 7 we can see that a low framework Si/Al ratio and low total conversion levels, both C_2/C_5 and C_3/C_4 ratios, are below 1. This is an indication that at least at low levels of conversion, the C_2/C_5 and C_3/C_4 ratios are not a measure of re cracking, since then there is no doubt that the $(C_2 + C_3)/(C_4 + C_5)$ ratio should be higher than 1. Moreover and from Figs. 6a and 7a it is again clear that comparing results at different lev-



SCHEME 7

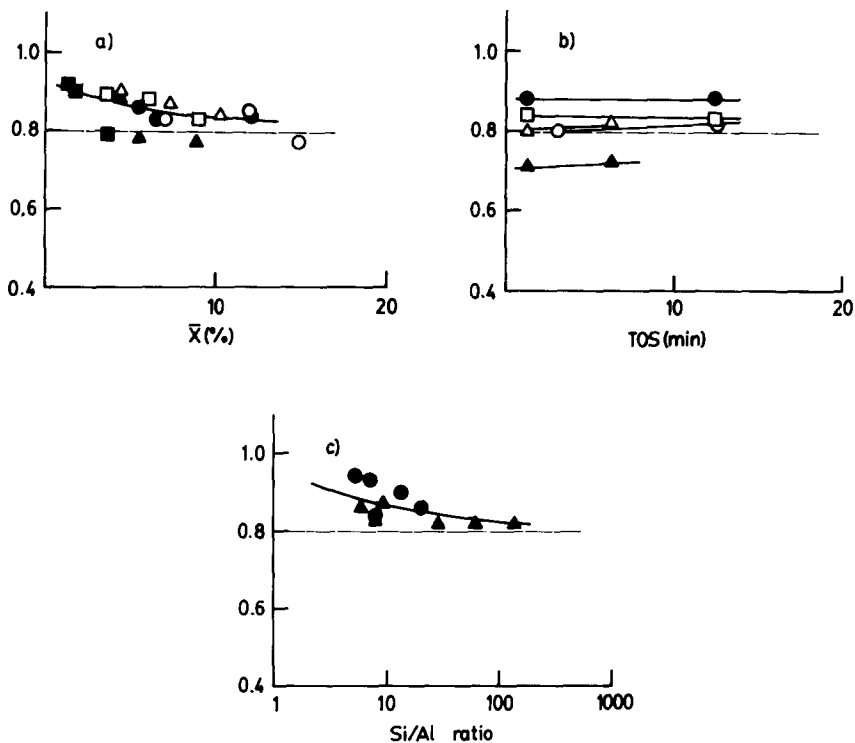


FIG. 5. The 2-methylhexane-to-3-methylhexane ratio in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1; (---), Thermodynamic equilibrium.

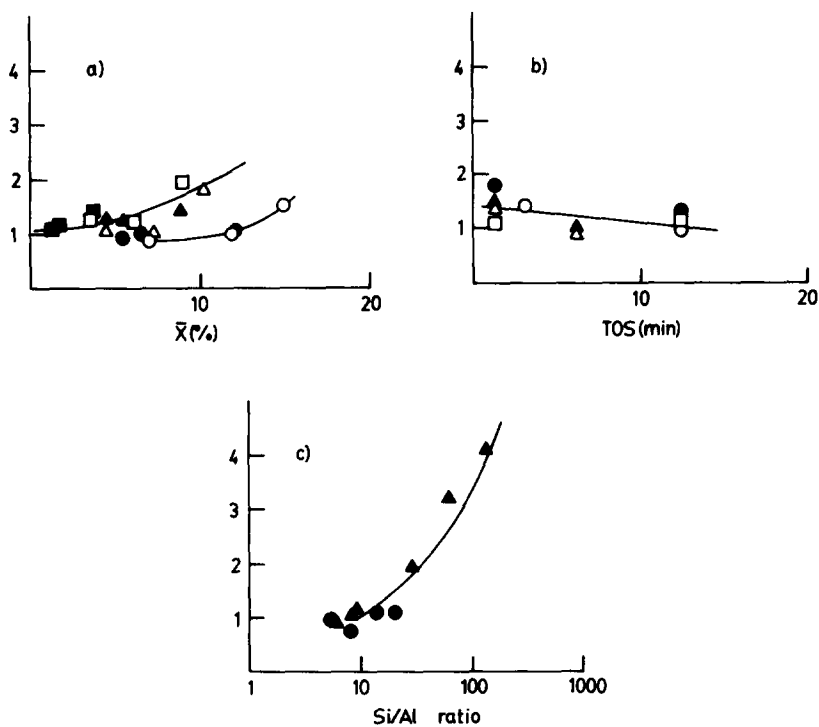


FIG. 6. C_2 -to- C_5 ratio in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1.

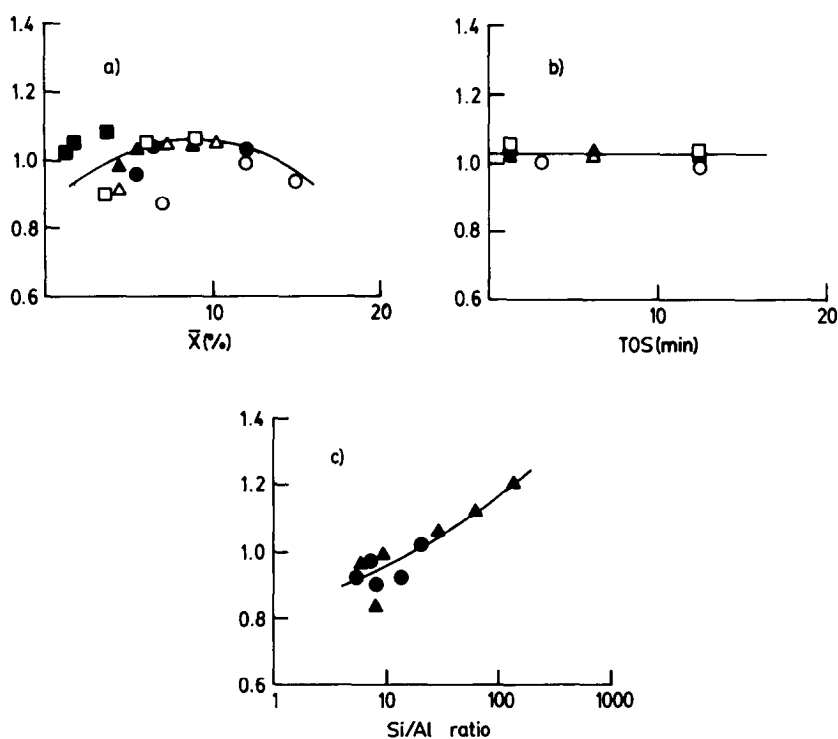


FIG. 7. C₃-to-C₄ ratio in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1.

els of conversion, even if conversions are relatively close, could be misleading. When increasing the framework Si/Al ratio both the C₂/C₅ and the C₃/C₄ ratios increase and for high Si/Al ratio they are above 1, showing that the very strong acid sites present, at these framework compositions, are much better catalysts for cracking of C₇ and re-cracking of C₆, C₅, especially of the branched, and even C₄, than those for carrying out disproportionation (condensation–re-cracking) and branching–isomerization reactions.

On the other hand, in Table 2 it can be seen that in zeolites dealuminated with SiCl₄, the selectivity changes in the C₁, C₂ fractions and the branched products are not very important. These changes can be explained by taking into account the shifts in the strength of acid sites. On the contrary, in steamed HYUS zeolites the selectivities of C₁ and C₂ fractions increase and the se-

lectivity of branched isomers decreases when the Si/Al ratio increases. These last results cannot be explained by considering only the strength of acid sites, since in very dealuminated zeolites (Al/uc ≤ 10) this variable should not be modified with the Si/Al ratio. Moreover in Table 2 it can be seen that with zeolites having ≈ 1 Al/uc the selectivity values of HYD catalyst are typical of a carbenium ion mechanism, while in HYUS catalyst the results show the participation of a cracking mechanism via free radicals, which should increase the ethane and ethylene selectivities and decrease the branched product selectivity. Consequently and taking into account the differences existing between the two zeolites, we think that these reactions via free radicals can be catalyzed by the species associated with the extra framework aluminum, probably as electron acceptor sites.

In Figs. 6 and 7 it can be observed that

TABLE 2
 Selectivities of Methane, Ethane, Ethylene, and $i\text{-C}_4/t\text{-C}_4$, $i\text{-C}_5/n\text{-C}_5$ Ratios
 over Different HYUS Catalysts at 450°C

\bar{X} (%)	Methane	Ethane	Ethylene	$i\text{-C}_4/t\text{-C}_4$	$i\text{-C}_5/n\text{-C}_5$	Catalyst
0.41	0.21	0.48	0.61	0	0	HYUS-5
0.58	0.17	0.39	0.48	0.21	0	
1.80	0.08	0.18	0.22	0.36	1.18	
0.43	0.15	0.31	0.39	0.23	0.42	HYUS-4
0.73	0.12	0.27	0.33	0.29	0.49	
4.30	0.03	0.07	0.08	0.43	1.67	
1.00	0.08	0.14	0.19	0.45	1.59	HYUS-2
1.72	0.04	0.07	0.10	0.46	1.87	
3.88	0.02	0.03	0.04	0.52	2.86	
1.52	0.03	0.07	0.08	0.48	1.57	HYD-5
4.69	0.02	0.05	0.06	0.50	1.68	
6.18	0.02	0.03	0.04	0.55	2.12	HYD-4
5.91	0.02	0.02	0.03	0.57	2.22	HYD-3
5.57	0.02	0.03	0.04	0.57	2.28	HYD-1

TOS has no effect in the C_3/C_4 ratio. The decrease in the C_2/C_5 ratio is probably due to the faster poisoning of the stronger acid sites which are responsible for the re cracking of short-chain hydrocarbons. The C_2/C_5 ratio increases with total conversion, while the C_3/C_4 ratio shows a maximum, produced probably by the increase in the bimolecular reactions of disproportionation at high conversion levels.

The selectivity to aromatics is strongly dependent on total conversion as it should be in secondary products (Fig. 8a). The TOS also has a positive effect on aromatics (Fig. 8b), while dealumination reduces the selectivity to aromatics (Fig. 8c).

It should be taken into account that the necessary step for the formation of aromatics is the condensation of olefins, and this should be unfavorable with respect to the rupture of the condensed products when the Si/Al ratio and the strength of acid sites increase. This interpretation would be consistent with the lower disproportionation reactions observed at high Si/Al ratios, the lower hydrogen transfer, and the lower

amounts of coke formed during cracking when the dealumination of the zeolite catalyst increases.

The effect of the framework Si/Al ratio on the selectivity of the products formed during cracking of n -heptane on dealuminated zeolite Y and the extension of those effects are given in Table 3.

Octane Performance of the Gasoline Fraction in Gas-Oil Cracking

Feedstock type, catalyst type, and operation variables are the primary factors affecting the gasoline quality obtained in an FCC unit.

The results presented previously and those obtained with a HYUS zeolite at three temperatures can be used to predict the influence of catalyst composition and several operation variables on the ON of fluid catalytic cracked gasoline.

According to Figs. 1–8 the catalyst capacity of hydrogen transfer and branching decreases when the Si/Al ratio increases. Therefore if a gasoline pool with high RON is desired, a catalyst with high Si/Al ratio

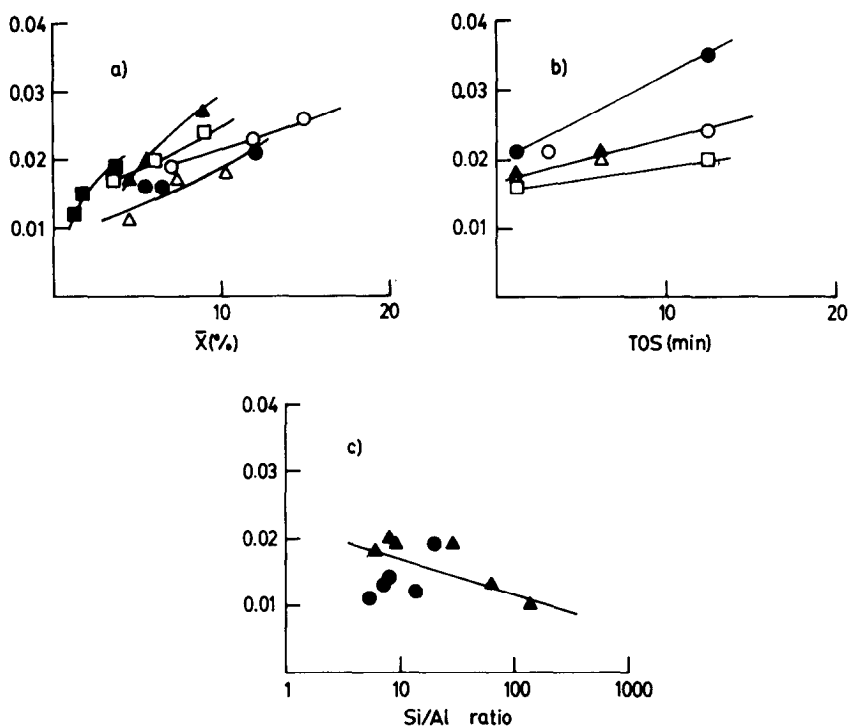


FIG. 8. Aromatic selectivity in HYUS and HYD zeolites vs total conversion, TOS, and Si/Al ratio. Symbols and conditions as in Fig. 1.

should be used, since in this case the olefin proportion will be increased. On the other hand, if a gasoline with a high motor octane number (MON) is required, a lower Si/Al ratio must be used because of the higher selectivity toward products that increase

the MON, such as aromatics and branched products.

The conversion also modifies the product selectivity because of its direct influence on secondary reactions. In Figs. 1–8, one can see that the hydrogen transfer and the

TABLE 3

Effect of the Si/Al Ratio (5.4–141) of the Dealuminated HY Zeolites on Product Distribution during Cracking of *n*-Heptane, at 5% Level of Total Conversion, 150 of TOS (*j*), and 450°C

	Increasing Si/Al	Limits of variation
Paraffin/olefin	Decreases	1.2–1.6
<i>i</i> -C ₄ / <i>t</i> -C ₄	No change	—
<i>i</i> -C ₅ / <i>t</i> -C ₅	Increases and then decreases	1.5–2
2 + 3MP/H	Decreases	Decreases until ≈2
2MH/3MH	Decreases up to equilibrium	0.96–0.86
C ₃ /C ₅	Increases	0.95–4
C ₃ /C ₄	Increases	0.90–1.2
Aromatic selectivity	Decreases	0.021–0.01

branching reactions increase with conversion. Therefore, since the amount of olefins diminishes and the amount of aromatics and branched products increases, an increase in conversion should cause a decrease in the RON and an increase in the MON. Nonetheless, the increase in the MON in gasoline thanks to an increase in conversion must be subject to an adequate economic balance. In this balance the loss of selectivity of the gasoline produced by re cracking at high conversions and the high cost of other processes for obtaining better quality in the gasoline (such as catalytic reforming, alkylation, use of blending agents) must be considered.

The time on stream (also called contact time) according to the data shown previously does not modify the proportion of olefins and increases the selectivity of aromatics and the branched products of C_5 and C_6 fractions. Consequently, high values of

this variable result in an increase in the MON and should not affect the RON, although as a drawback the coke level on the catalyst tends to increase.

The temperature is another factor affecting product selectivity and hence gasoline quality. The results presented in Fig. 9 correspond to different temperatures indicating that increases in this variable produce increases in the RON, because the proportion of olefins in the cracking products becomes greater. On the contrary, the higher the temperatures, the lower the MON as can be concluded from the decrease in the branched C_5 and C_6 fractions and from maintenance of selectivity toward aromatics.

Finally, it would be interesting to compare the behavior of the RON and the MON predicted in this work with that obtained in commercial units or pilot plants (18). In this last case, increases in the RON and the

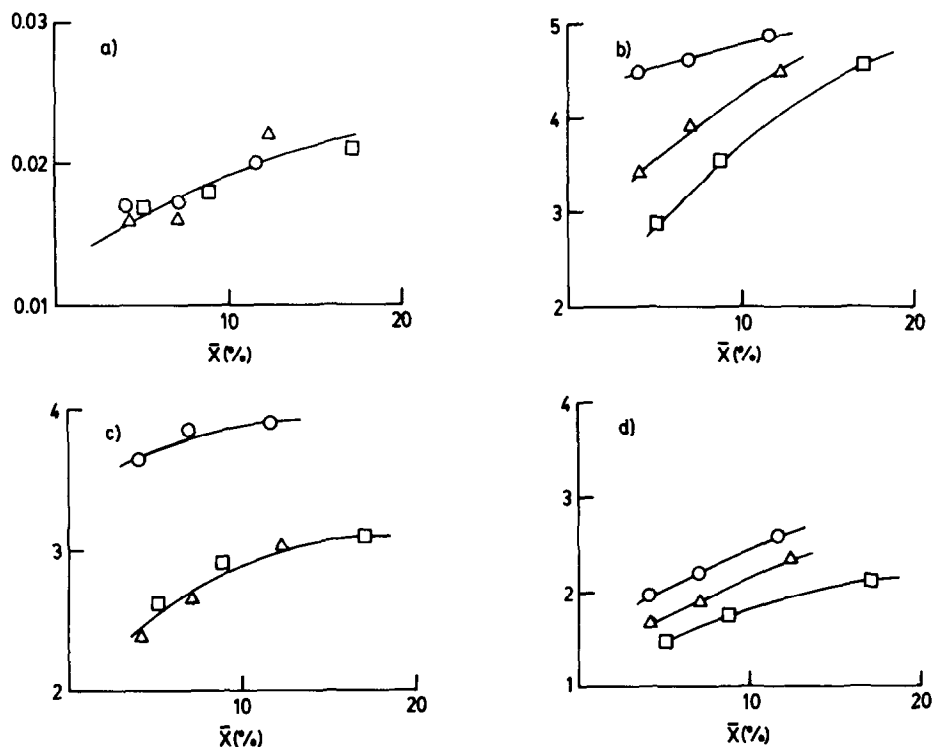


FIG. 9. Variation of selectivity with temperature in HYUS-2 zeolite. (a) Aromatic selectivity. (b) 2 + 3MP/H ratio. (c) $i-C_5/n-C_5$ ratio. (d) Paraffin/olefin ratio. (○) 430°C, (△) 450°C, (□) 470°C.

MON with conversion are observed, produced by increases in the aromaticity of the gasoline obtained (an unexpected result with regard to RON). Increases in the RON and the MON are observed with the catalysts that diminish hydrogen transfer reactions. According to our predictions, higher temperatures give higher RONs and do not modify the MON. Nonetheless, the difference observed between prediction and actual behavior of a commercial unit may be caused by the presence of naphthenes in feed and product streams of the FCC unit. It is known that the presence of naphthenes in the feed increases the proportion of olefins and aromatics, that the naphthene/paraffin ratio modifies the ON, etc.

CONCLUSIONS

—The hydrogen transfer reactions and therefore the P/O ratio is strongly dependent on the level of conversion, the P/O ratio being higher at higher conversions. This implies that if the hydrogen transfer abilities of different zeolites and in general of different cracking catalysts must be compared, the conversions must be maintained constant.

From the point of view of the zeolite catalyst the P/O ratio depends not only on the acid site density but also on the acid strength of the acid sites. The stronger the acid site, the higher the ratio of the cracking rate to the hydrogen transfer rate. In highly dealuminated zeolites (hydrophobic) the amount of olefins adsorbed will be proportionally smaller than the amount of paraffins, decreasing strongly therefore the rate of bimolecular reactions such as hydrogen transfer and disproportionation.

—In highly dealuminated zeolites the cracking reactions occurring on extra framework aluminum become important. The cracking on these sites takes place via a radical-type mechanism and will produce more C_1 , C_2 , and olefins than the cracking on the Brønsted acid sites.

—Most of the cracking of C_7 takes place

through the formation of branched carbenium ions, via secondary–tertiary, secondary–secondary, or tertiary–secondary carbenium ions. The stabilization of the different types of carbenium ions is a function of the acid strength, cavity dimensions of the zeolite, and reaction temperature.

—The $i-C_5/n-C_5$ ratio observed in the cracked products is above the thermodynamic equilibrium indicating that the $i-C_5$ does not come from the branching of $n-C_5$ but mainly through disproportionation reactions. A maximum $i-C_5/n-C_5$ ratio is observed and therefore the disproportionation depends on the framework Si/Al ratio of the zeolite with the maximum located at ~ 10 .

—The longer the hydrocarbon chain in the products, i.e., C_5 , C_6 , C_7 , the lower the ratio of branched to unbranched isomers is. Moreover, for a given hydrocarbon chain the higher the strength of the acid sites the lower will be the ratio of branched to unbranched isomers.

—The selectivity to aromatics increases with total conversion and with time on stream, while the dealumination reduces the selectivity to aromatics.

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