Influence of Framework Aluminum Gradients on the Catalytic Activity of Y Zeolites: Cracking of Gas-Oil on Y Zeolites Dealuminated by Different Procedures

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The catalytic cracking of gas-oil has been studied in a series of REHY and HY zeolite catalysts dealuminated by "deep bed" calcination, steaming, and SiCl₄ treatment. The samples have been characterized by X-ray diffraction, pyridine adsorption, and X-ray photoelectron spectroscopy (XPS). It has been found that the framework Si/Al ratio determined by XPS (surface Si/Al) and that determined from unit cell dimension measurements (bulk Si/Al) differ, indicating a gradient in the concentration of the framework aluminum normal to the surface of the zeolite crystallites. When the gas-oil cracking activity is plotted versus unit cell dimension, three different volcano curves are obtained, with activity maxima located at about 24.59, 24.35, and 24.33 Å for deep bed, steamed, and SiCl₄-treated zeolites, respectively. These results, together with the behavior of the selectivity curves to gasoline, light cycle oil (LCO), gases, coke, and butene/butane ratio, are discussed on the basis of Si/Al gradients. Comparison of the cracking behavior of a short molecule such as n-heptane with that of gas-oil, in relation to the acidity of the samples measured by pyridine adsorption, supports the idea that gas-oil does not penetrate the zeolite deeply and, therefore, that the activity of the catalyst is controlled by the framework Si/Al ratio close to the external surface, instead of the bulk Si/Al ratio of the zeolite crystallites. © 1987 Academic Press, Inc.

INTRODUCTION

In many catalytic processes the most important property to be achieved during catalyst preparation is a large number of accessible active sites. In cracking catalysts, this activity criterion can be swamped by others, such as catalyst thermal and hydrothermal stability and catalyst selectivity, which in a long-term operation can be more decisive than conversion itself. This can be understood if one considers that during the cracking of gas-oil and residues a successful commercial catalyst should have a high selectivity for gasoline and light cycle oil (LCO), low gas and coke yield, and a high yield of olefins and branched hydrocarbons which increase the gasoline octane number. Furthermore, the

catalyst should be stable enough to withstand the drastic thermal and hydrothermal conditions of the regeneration step (1–3).

Most of these properties have been achieved by the introduction of ultrastable HY (USY) and rare-earth (RE)-exchanged ultrastable HY zeolites (REUSY) (4). These zeolites have in common, besides the open structure of the parent Y zeolites, a relatively high framework Si/Al ratio. The value of the Si/Al ratio in the starting NaY zeolite is 2.4, while the value for the final ultrastable Y sample can be as high as 20 or more.

The dealumination of the zeolite can be achieved by "deep bed" calcination of exchanged samples (5), acid leaching (6), SiCl₄ treatment (7), and heating of the exchanged zeolite in the presence of steam (8) or mixtures of air and steam. In any case, the control of the framework Si/Al ratio is a key point in controlling activity, selectivity,

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and stability (9–11). Indeed, the activity and selectivity are a function of the framework Si/Al ratio, since this ratio controls the total number, density, and strength distribution of the acid sites. On the other hand, it is known (3) that the higher the Si/Al ratio in the Y zeolite, the higher its thermal and hydrothermal stability.

Recently (9) an interesting work on gas-oil cracking on commercial zeolite catalysts was reported. A correlation of activity and selectivity with the framework Si/Al ratio estimated from the unit cell dimensions was established for a short range of values (24.24–24.30 Å).

In the present work, a series of Y zeolites within a range of unit cell dimensions from 24.27 to 24.70 Å, achieved by different preparation procedures, has been obtained. The behavior of these zeolites for gas-oil cracking is discussed on the basis of their framework and surface Si/Al ratio surface acidity, and method of dealumination.

EXPERIMENTAL

Three series of Y zeolites, with a range of unit cell dimensions from 24.24 to 24.70 Å, were prepared from a SK-40 NaY (Si/Al = 2.4) with a unit cell of 24.72 Å, by the following procedures:

(1) A series of LaHY zeolites was obtained by exchanging part of the Na^+ with La^{3+}, and then the remaining Na^+ with NH_4^+. The levels of Na^+ exchanged with La^{3+} were 0, 15, 40, 68, and 82% of the original one, and the samples were designated REHY-0, REHY-1, REHY-2, REHY-3, and REHY-4, respectively. The samples were deep-bed calcined at 550°C after exchange, and in this way unit cell dimensions in the range 24.40–24.70 Å were achieved.

(2) A second series of LaHY zeolites was obtained by steaming the REHY samples at 750°C and 1 atm of water pressure for 3 h. The unit cell dimensions of the steamed zeolites were in the range 24.31–24.58 Å and they were named SREHY-n.

(3) Finally, a third series of samples was

obtained by treatment of the starting NaY (SK-40) with $SiCl_4$, following the procedure described by Beyer et al. (7). The dealuminated samples, designated HYD-n, were washed until no Cl^- was detected in the wash water. They were then exchanged with NH_4^+ ions and calcined at 550°C. The exchange–calcination procedure was repeated three times until practically no Na^+ was detected in the wash water. In this case the unit cell dimension range achieved was 24.30–24.43 Å. One of the samples, HYD-4 (24.30 Å), was steamed at 800°C for 3 h and the unit cell of the resulting zeolite (SHYD-4) was 24.27 Å.

A vacuum gas-oil was used as reactant, and the characteristics of the feed are given in Table 1.

The catalytic experiments were carried out in a fixed bed glass tubular reactor at atmospheric pressure, heated at 482°C by an electrical furnace divided into three heating zones. Prior to each experiment the catalyst was flushed with N_2 at reaction temperature for 20 min. Then, the reactant was charged at the top of the reactor by means of a constant-rate positive-displacement pump. Thermal effects during the

TABLE 1

Characteristics of Vacuum-Distilled Gas-Oil

Distillation curve		Physicochemical properties	
wt%	°C		
IP^a	240	Density, API (15°C)	26.3
5	307	Conradson index (wt%)	0.14
20	332	Hydrogen (wt%)	11.9
30	345	Sulfur (wt%)	2.14
40	362	N_2 (ppm)	562
50	378	K-UOP	11.5
60	390	Freezing point (°C)	24
70	405	Pensky Martens (°C)	130
80	420	Viscosity (C.S.) 40°C	11.54
90	445		
95	465		
FP^b	512		

^{a} Initial point.
^{b} Final point.

reaction were minimized by diluting the zeolite catalyst (0.59–0.84 mm in diameter) with silica (BASF, 0.25–0.42 mm in diameter) up to 8 ml of final volume.

A given amount of gas-oil (8.4 g) was fed at different space velocities in the range 15–300 h^{-1} by changing the speed of the pump, in order to carry out several experiments with different times on stream (t_f). During the reaction, the liquid products were trapped in a pot after passing through a condenser located below the reactor, while the gaseous products were trapped by the downward displacement of water in gas burettes. At the end of each run the reactor was purged with N_2 for 15 min and the purged gases were collected for analysis. Finally, the catalyst was regenerated by burning off the coke with a 7 liter h^{-1} stream of air at 520°C for 6 h. The gases of combustion were passed through a CuO furnace heated at 400°C to convert the CO to CO_2.

Liquid and gaseous products were analyzed by gas chromatography. Gasoline and LCO fractions were taken at 210 and 300°C, respectively. The amount of coke deposited on the surface of the catalyst was determined by measuring the amounts of H_2O and CO_2 adsorbed on Drierite and Ascarite, respectively. The catalyst-to-oil ratio was varied by changing the amount of zeolite in the reactor. Catalyst-to-oil ratio is defined as the amount of catalyst in grams divided by the 8.4 g of gas-oil passed through.

Thermal cracking accounts for less than 1% of the total conversion. The closed system allows mass balances to be made, and only experiments with mass balances of 100 ± 5% were considered.

In previous work (12), a full kinetic study of gas-oil cracking was carried out. It was found that with this feed and this type of catalyst the conversion data were best fitted by a pseudo-first-order kinetic equation instead of by a second-order equation (13) or by one with an order higher than 2. Therefore, the activity of the zeolite catalysts presented here was calculated assum-

ing a pseudo-first-order rate constant for the conversion obtained at 2.0 min time on stream and a weight space velocity of 2.4 min^{-1}. The pseudo-first-order rate constant has been obtained with a relative error of 5%.

The unit cell constant of the zeolites was determined by X-ray diffraction using Cu$K\alpha$ 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 peak heights of the (5,3,3) peak, and considering the NaY SK-40 at 100% crystallinity (14).

Infrared spectroscopic measurements of adsorbed pyridine were carried out in a conventional greaseless IR cell. Wafers of 10 mg cm^{-2} were pretreated overnight at 400°C and 1.33 × 10^{-3} Pa of dynamic vacuum. Then, 6.66 × 10^2 Pa of pyridine was introduced into the cell at room temperature. After equilibrium the samples were outgassed at 350°C under vacuum, and the spectra recorded at room temperature in a Perkin–Elmer 580B spectrophotometer equipped with a data station. The area of the bands at 1545 and 1450 cm^{-1} was measured and from these values and the extinction coefficients for these bands given by Hughes and White (15), the amount of Brønsted and Lewis acid sites was calculated.

RESULTS

In Table 2, the crystallinity of the different zeolites, the unit cell constant values, and the calculated bulk framework Si/Al ratio (16) are given, while in Table 3 the bulk and surface framework Si/Al ratios are compared for various zeolites. It can be seen that when the La^{3+} content in the zeolite increases, the shrinkage of the unit cell dimension is lower, which indicates that the dealumination by steaming decreases.

The gas-oil cracking activity divided by the crystallinity of the sample is plotted versus the unit cell dimension for three

TABLE 2

Crystallinity and Unit Cell Size of the
Different Zeolites

Sample	RE$_2$O$_3$ (wt%)	Crystal- linity (%)	Unit cell size (Å)	Si/Al ratio[b]
REHY-0	—	55	24.40	9.0
REHY-1	3.3	63	24.46	6.5
REHY-2	8.3	64	24.59	3.8
REHY-3	12.8	68	24.68	2.8
REHY-4	17.3	63	24.70	2.5
SREHY-1	3.3	46	24.31	21.0
SREHY-2	8.3	43	24.38	10.5
SREHY-3	12.8	53	24.51	5.0
SREHY-4	17.3	61	24.58	3.9
HYD-1		48	24.43	7.6
HYD-2		71	24.39	9.8
HYD-3		75	24.35	13.6
HYD-4		71	24.30	24.5
SHYD-4		51	24.27	45.0

[a] REHY-n, deep bed zeolites; SREHY-n, steamed zeolites; HYD-n, zeolites HY-dealuminated with SiCl$_4$; SHYD-4, zeolite treated with SiCl$_4$ then steamed.

[b] Calculated from unit cell sizes using the procedure described in Ref. (16).

series of zeolites in Fig. 1. Three different curves are obtained depending on the catalyst preparation procedure with activity maxima in the range 24.54–24.60 Å for the
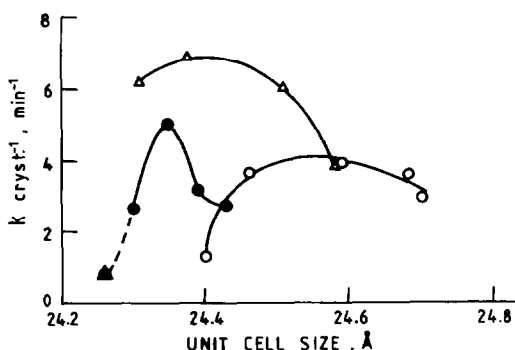
deep bed calcined samples, and 24.37–24.43 and 24.31–24.37 Å for steamed and SiCl$_4$ dealuminated samples, respectively, corresponding (16) to framework Si/Al ratios of 3.7–4.6, 7.8–11.5, and 11.5–21.2, respectively.

The selectivity plots for the reaction products considered, i.e., gasoline, LCO, total gases, C$_1$ + C$_2$, coke and butene/ butane ratio, are presented in Figs. 2a–f, respectively. With decreasing unit cell dimension, the selectivity to gasoline for deep bed calcined zeolites decreases; that for steam-dealuminated samples increases up to a value of ~24.35 Å and then decreases; and that for SiCl$_4$-treated zeolites slightly decreases up to ~24.35 Å, then increases for the 24.30 Å sample, and sharply decreases for samples with lower values of unit cell dimension. The relationship between selectivity to LCO and unit cell dimension follows the same trend as that of total activity. For deep bed zeolites the selectivity to coke increases with decreasing unit cell size, while for SiCl$_4$ and steam-dealuminated samples it decreases. The selectivity to gases increases when the unit cell size decreases, except for the HYD series for which it is a minimum at ~24.30 Å and then increases sharply.

The butene/butane ratio, which is directly proportional to the RON of the gasoline produced (17), increases with decreasing unit cell dimension in the three series of zeolites.

FIG. 1. Effect of zeolite unit cell size on gas-oil cracking activity for dealuminated Y zeolites: deep bed (○), steamed (△), SiCl$_4$-treated (●), steamed after SiCl$_4$ treatment (▲).

TABLE 3

Surface and Bulk Framework Si/Al Ratios of Some
Dealuminated Zeolites

Sample	Bulk Si/Al ratio[a]	Surface Si/Al ratio (XPS)
REHY-1	6.5	2.4
HYD-1	7.6	2.4
HYD-2	9.8	3.8
HYD-4	24.5	4.5

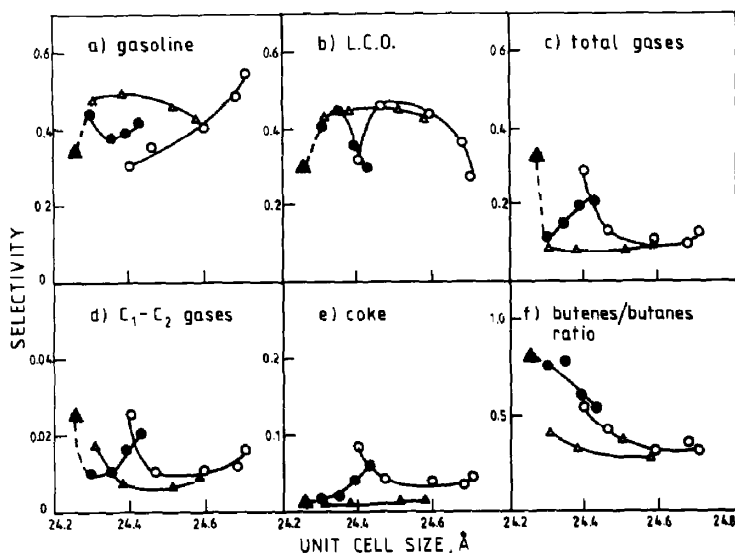[a] Calculated from unit cell sizes using the procedure described in Ref. (16).

FIG. 2. Effect of zeolite unit cell size on gas-oil cracking selectivities for dealuminated Y zeolites: deep bed (O), steamed (△), SiCl₄-treated (●), steamed after SiCl₄ treatment (▲).

DISCUSSION

Influence of Si/Al Ratio and Zeolite Activation Method on Gas-Oil Conversion

It has been shown (9, 11, 18) that the activity for alkane cracking can be correlated with the strongest acid sites of the zeolites. From the model of acid strength distribution in zeolite Y presented by Pine et al. (9), a maximum in the concentration of strong acid sites is found for a zeolite with a uniform distribution of aluminum along the crystal and with a unit cell dimension of 24.47 Å. Therefore, if the activity is related with the amount of strong acid sites and this is a direct consequence of the Si/Al ratio in the Y zeolite, or, equivalently, of the unit cell dimension, one should expect that this parameter could be used as a criterion to predict the cracking activity of a given Y zeolite (9).

Nevertheless, we must take into account that the Si/Al ratio measured from unit cell dimensions or by high-resolution magic-angle spinning solid-state ^{29}Si and ^{27}Al NMR is an average for the crystal. On the other hand, it has been shown that the

composition of the outer surface differs from that of the bulk as a consequence of a nonuniform dealumination (19). More specifically, dealumination by steaming or by treatment with SiCL₄ produces aluminum surface-rich samples (20). If this is so, and taking into account that for a zeolite with crystallite sizes in the range 1-2 μm, as is our case, gas-oil molecules do not have access to the entire internal surface (21, 22), it is clear that the average values of the framework Si/Al ratio based on a uniform Si/Al distribution along the crystal cannot be the unique criterion on which to predict gas-oil cracking activity on zeolite samples with nonuniform dealumination. Indeed, different procedures (deep bed calcination, steaming, steaming + leaching, SiCl₄, etc.) will probably produce for the same bulk framework Si/Al ratio different framework Si/Al gradients normal to the surface of the zeolites. This gradient, however, decreases and eventually disappears for samples that are sufficiently dealuminated.

We have measured by an XPS procedure, which allows us to distinguish between tetrahedrally and octahedrally coordinated aluminum (23), the framework

Si/Al ratio of the surface of the crystallites. The values are compared with the bulk Si/Al ratio calculated from the unit cell dimension in Table 3. The strong differences between the values in the external part of the crystal and in the bulk indicate that, indeed, there must be a strong gradient in the Si/Al ratio normal to the crystal surface. Moreover, the dealumination occurs preferentially inside the crystallites. This type of gradient cannot be explained by a simple mechanism in which either chemical reaction or diffusion is the controlling step in the dealumination process. Indeed, when the chemical reaction is the controlling step, a uniform distribution of the aluminum along the crystal is expected, while when diffusion is controlling, a preferential dealumination of the crystal surface should be obtained. The observed Si/Al gradient can be explained either by realumination of the surface or by assuming that during the dealumination process there is a thermal gradient inside the crystallites due to the strong exothermicity of the reaction. Then, since the dealumination involves activation energies of the order of 100 kcal mol^{-1} (14), one would expect that the reaction would proceed further at points more distant from the external surface.

Another difference that can be observed when comparing the curves corresponding to the steamed and SiCl$_4$-dealuminated samples is that, besides the fact that the HYD curve lies below the SREHY curve, the differences in activity among the SiCl$_4$-treated samples are higher than the corresponding differences among the steamed samples. In the last case, besides the possible differences in the Si/Al gradient, there are other factors such as the presence of extra-framework aluminum and the presence of mesopores in the steamed samples, both less important in the SiCl$_4$-treated samples. This difference can play an important role in behavior of the catalysts since the mesopores facilitate the diffusion of large molecules, while the extra-framework aluminum can block cavities as well as catalyze nonselective cracking.

Influence of Si/Al Ratio and Zeolite Activation Method on Selectivity

Recently (2), a "PacMan"-type process for cracking of gas-oil was presented. In this process the first step of the paraffinic gas-oil cracking is the formation of a short-chain olefin by β scission inside the zeolite pore, and of a long-chain carbocation attached to a site relatively near the entrance of the pore. The carbocation can either undergo further reaction or desorb and diffuse out of the pore structure. The short-chain olefin, on the other hand, lies deeper inside the pore structure, and spends a considerable amount of time inside the channels of the zeolite, encountering active sites and giving secondary reactions. From the model described above it is evident that the gas-oil conversion of a given zeolite will be controlled by the Si/Al ratio of the framework close to the surface, while the selectivity will also depend on the Si/Al ratio in the innermost part of the zeolite crystallite. Then, one should expect that in the first cracking event the long-chain carbocation formed in the more external part of the pore, and which can desorb, will still correspond to a gas-oil molecule or, more frequently, to a LCO molecule.

Therefore, at conversion levels lower than 60%, where recracking is not very important, the plot of selectivity for LCO versus unit cell dimension should follow a pattern similar to that for gas-oil cracking. This is indeed observed in Fig. 2b. However, the molecule of gasoline or gas formed in the first cracking event, which will diffuse in the interior of the pore system of the zeolite, can suffer recracking, hydrogen transfer, isomerization, cyclization, etc., which will finally give a selectivity pattern that will also depend on the Si/Al ratio in the interior of the crystallite. Here, the selectivities obtained at similar levels of conversion (60%) and short time on stream (2 min) with catalysts of different

unit cell dimensions are considered. Then, the higher the Si/Al ratio, the less favored will be bimolecular reactions such as those involved in coke formation and hydrogen transfer. Therefore, the selectivity to coke should decrease as the unit cell size decreases, at least for values ≤ 24.40 Å for which the amount of any type of acid sites decreases as the unit cell dimension decreases, as can be observed in Fig. 2e. The opposite should occur with the olefin/paraffin ratio, since olefins are saturated by hydrogen transfer. Indeed, the butene/butane ratio increases when unit cell size decreases, indicating that the RON of the gasoline should increase with decreasing unit cell dimension of the Y zeolites.

Moreover, it is known that increasing the Si/Al ratio increases the acid strength of the zeolite (9, 24–28). Hence, one would expect that cracking near either end of the primary formed hydrocarbons would become more probable, increasing the selectivity to gases when the unit cell decreases. This effect would be more marked for the formation of shorter gas molecules, which are mostly secondary products, as is ob-

served in Figs. 2c and d. The gasoline molecule formed can isomerize, become saturated, or recrack, depending on the density and strength of the acid sites encountered. Cracking of short-chain hydrocarbons which form the gasoline fraction requires, in principle, stronger acid sites than cracking of the longer chain molecules of the gas-oil. Therefore, as very strong acid sites are formed at high Si/Al ratios, the gasoline would readily recrack inside the crystallites, giving gases and decreasing the selectivity to gasoline (Fig. 2a).

Relation between Cracking Activity and Acidity Measured by Pyridine Adsorption

Pyridine adsorption is generally used as a procedure to measure the amount and nature of acid sites on solid catalysts. In the case of Y zeolites, this molecule is very useful since it can easily penetrate inside the supercages, and gives a reliable measure of the concentration of acid sites. Furthermore, by thermal desorption of the pyridine it is possible to estimate the acid strength distribution. Therefore, pyridine

TABLE 4

Cracking Activity of the Dealuminated Zeolites for n-Heptane and Gas-Oil

Sample	Cracking activity[a]		AS^b (Py μmol g^{-1})	k_{hep}/AS ($\times 10^3$)	$k_{gas\text{-}oil}/AS$ ($\times 10^2$)
	$k_{n\text{-heptane}}$ (m^3 s^{-1} kg^{-1} cat)	$k_{gas\text{-}oil}$ (s^{-1})			
REHY-0	0.22	1.2	130	1.7	0.9
REHY-1	0.40	3.7	143	2.8	2.6
REHY-2	0.25	3.9	124	2.0	3.1
REHY-3	0.21	3.7	111	1.9	3.3
REHY-4	0.19	3.0	86	2.2	3.5
SREHY-1	0.06	6.2	17	3.5	36.5
SREHY-2	0.09	6.9	27	3.3	26.5
SREHY-3	0.07	6.1	31	2.3	19.7
SREHY-4	0.05	3.8	25	2.0	15.2
HYD-1	0.15	2.8	110	1.4	2.5
HYD-2	0.16	3.0	108	1.5	2.8
HYD-3	0.19	5.2	86	2.2	6.0
HYD-4	0.06	2.7	57	1.1	4.7
SHYD-4	—	0.8	—	—	—

[a] All constants have been calculated taking into account the crystallinity of the samples.
[b] Acid sites.

can measure the acidity responsible for the cracking of short-chain hydrocarbons which can easily penetrate deep inside the crystallites of the zeolite; however, the acidity measured by pyridine cannot be representative of the surface "seen" by a long chain of gas-oil if the framework Si/Al ratio is not uniform along the crystallite.

To check the effect of an inhomogeneous Si/Al ratio, the activities for cracking of the small hydrocarbon molecule n-heptane (29) have been related to the amount of strong acid sites that retain pyridine under 350°C and 1.33×10^{-2} Pa desorption conditions. In Table 4 it can be seen that the higher the amount of strong acid sites in a series of catalysts, the higher is the activity of the catalyst for n-heptane cracking. In the same table no direct correlation is observed between the acidity measured by pyridine and activity for gas-oil, if catalysts prepared by different procedures are compared. Indeed, the steamed samples present a higher activity per acid site than the other zeolites, which can easily be explained by considering that more acid sites will be available to the large gas-oil molecules in the steamed samples due to the higher secondary mesopore structure formed during steaming. This result shows the importance of diffusion in the case of the gas-oil, where the primary reactivity must be restricted to a small outer shell of the zeolite.

ACKNOWLEDGMENTS

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