JOURNAL OF CATALYSIS 122, 230–239 (1990)

Hydrogen Transfer on USY Zeolites during Gas Oil Cracking: Influence of the Adsorption Characteristics of the Zeolite Catalysts

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Received February 3, 1989; revised October 11, 1989

In this work, the hydrogen transfer activity of two series of HY zeolites dealuminated by steam and by $SiCl_4$ (24.47–24.24 Å unit cell) has been measured from the butene/butane ratio in the products obtained during the cracking of a vacuum gas oil at 756 K. With the steam-dealuminated zeolites, a sharp decrease in the ratio of hydrogen transfer to cracking is observed when the number of Al atoms per unit cell falls below 10. On the other hand, in samples dealuminated by $SiCl_4$, this ratio changes very little with dealumination. These results cannot be explained assuming the need for adjacent acid sites for the hydrogen transfer. We have found, by adsorption measurements of *n*-butane and 1-butene, that the changes in the relative rates of bimolecular (hydrogen transfer) to monomolecular (cracking) reactions, observed with dealuminated HY zeolites, can be explained by the changes in the adsorption capacity and adsorption selectivity which occur on zeolites dealuminated at different levels by different dealumination procedures, and which are due to changes in the electric fields inside the pores. © 1990 Academic Press, Inc.

INTRODUCTION

The mechanism of catalytic cracking has been a matter of discussion since the early sixties. Detailed mechanisms have been written starting from different hypotheses (*1–4*) and the reaction pathways have been studied by means of MO and isotopic techniques (*4–6*). However, it is known that during catalytic cracking of gas oil, other reactions, besides C–C bond breaking, take place (*7*), which in some cases can determine the quality of the resultant gasoline. One of these important reactions is hydrogen transfer. Indeed, it is accepted that this reaction is responsible for saturation of olefins, probably (*8, 9*) through reactions of the type

olefin + cycloalkane → paraffin + aromatic.

The saturation of olefins produces a decrease in the research octane number (RON), which cannot be compensated by the formation of aromatics. In spite of its importance, little is known about the details of how the different parameters of the zeolite may influence the reaction.

It has recently been proposed (*10*) that the main factor controlling the hydrogen transfer of Y zeolites during the cracking of gas oil is the density of aluminum, i.e., the density of Brønsted acid sites. The higher the density, the higher the hydrogen transfer rate. It was assumed (*10*) that hydrogen transfer is a bimolecular reaction which requires the presence of two close acid sites. By dealumination, the distance between sites increases, and therefore the hydrogen transfer reactions decrease. However, if one considers the necessity of two close acid sites for hydrogen transfer to take place, it is not possible to explain why the saturation of olefins still decreases when the number of aluminums per unit cell (UC) is reduced from 3 to 1 or even less. Furthermore, the reported assumption can neither explain the fact that samples of zeolite USY with the same number of aluminums per UC, but obtained by different dealumina-

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0021-9517/90 $3.00
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TABLE 1

Physicochemical Characteristics of the Zeolite Samples

Sample	a_0 (Å)	Framework Si/Al ratio	Number of Al/UC	Crystallinity (% SK-40)	H_2O[a] (wt%)	S_{BET} ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Pore volume <10 Å ($cm^3\ g^{-1}$)
HYS-1	24.27	6	27	90	8.9	508	0.41	0.24
HYS-2	24.31	21	9	84	4.6	541	0.56	0.27
HYS-3	24.28	35	5	85	3.5	472	0.48	0.23
HYS-4	24.26	62	3	76	3.0	534	0.58	0.27
HYS-5	24.25	95	2	75	3.5	495	0.60	0.25
HYS-6	24.24	136	1.4	60	3.4	393	0.57	0.20
HYD-1	24.47	6	27	100	7.8	533	0.38	0.28
HYD-2	24.43	8	22	100	7.2	630	0.44	0.32
HYD-3	24.35	10	13	86	7.4	587	0.38	0.25
HYD-4	24.25	95	2	85	3.6	446	0.37	0.22

[a] Total amount adsorbed at 373 K and 22 Torr.

tion procedures, give a different ratio of cracking to hydrogen transfer.

In this work we present both adsorption and catalytic cracking results on HY zeolites dealuminated by different procedures. It is shown that the changes in adsorption capacity and adsorption selectivity (for olefins and paraffins) due to dealumination have a clear influence on the hydrogen transfer behavior during cracking of gas oil.

EXPERIMENTAL

Two series of dealuminated HY zeolites were obtained by dealumination of a SK-40 zeolite (Si/Al = 2.4) by steam (HYS) and $SiCl_4$ (HYD) treatment, following the procedures described previously (*11*). The physicochemical characteristics of the samples are given in Table 1.

Catalytic runs were performed in a fixed-bed glass tubular reactor at 756 K. The zeolite catalysts were pelletized, crushed, and sieved, and the fraction 0.84–0.59 mm was selected. The conversion was changed by modifying the catalyst-to-oil ratio in the range of 0.05–0.28 g/g. Time-on-stream was kept constant at 60 s in all experiments, since as can be deduced from previous results (*12*), this time-on-stream falls in the optimum performance envelope (*13*). In this way it was possible to obtain curves of yield versus conversion, and to compare selectivities, during gas oil cracking at the same level of conversion, as has been recommended in the literature (*12, 14*).

The surface area and pore size distribution of the catalysts were calculated from the N_2 adsorption–desorption isotherms carried out in a volumetric system (Sorptomatic 1800 Carlo Erba) at 77 K. Adsorption isotherms for *n*-butane and 1-butene were obtained in a Cahn recording microbalance connected to a greaseless conventional vacuum system with a dynamic vacuum of 10^{-6} Torr. The adsorption experiments were performed as follows: the zeolite samples were carefully crushed, and the fraction smaller than 200 mesh was placed in a glass pan. The zeolite was then evacuated at 10^{-4} Torr, and dehydrated by slowly raising the temperature to 723 K until there was no further weight loss. After equilibration of the zeolite at the adsorption temperature the adsorbate was admitted and the pressure recorded. Equilibrium was considered to have been achieved when the changes in weight were smaller than 0.2% in 1 h. To prevent surface modifications due to the possibility of polymerization or coke formation, a fresh sample of zeolite was used in each experiment.

The purity of the gases used was higher than 99%, and the characteristics of the gas oil have been reported previously (*15*).

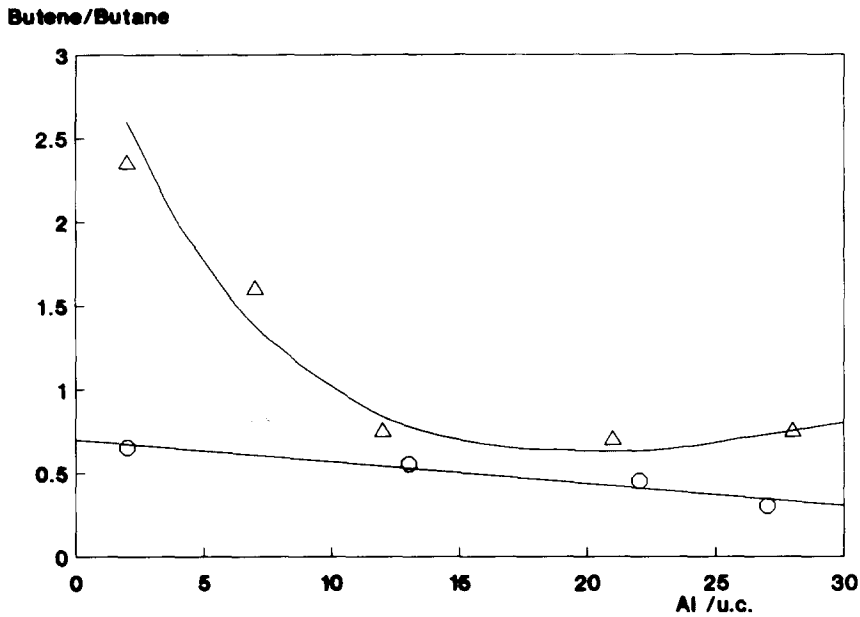

FIG. 1. Butene/butane ratio obtained during the cracking of gas oil at 65% conversion on HYS (△) [taken from (*11*)] and HYD (○) zeolites at 723 K.

RESULTS AND DISCUSSION

It has been shown (*10*), for the cracking of gas oil on catalysts containing Y zeolite, that by decreasing the number of aluminums per unit cell, i.e., by increasing dealumination, the amount of olefins in the gasoline obtained increases and, therefore, its RON increases. It has also been shown that the degree of olefinicity of the gasoline obtained when cracking gas oil corresponds very well with the olefinicity of the C_4 fraction (*16*). Figure 1 shows the butene/butane ratio obtained at 65% conversion when cracking gas oil on the HYS and HYD zeolite samples. Two major features can be observed here: First, the butene/butane ratio in the steam-dealuminated HYS samples remains quite constant with dealumination up to ≈10 Al per unit cell, and then increases sharply upon further decrease of the framework Al content. However, for the $SiCl_4$ dealuminated samples, the butene/butane ratio remains unchanged by dealumination. Second, while the values for the olefin-to-paraffin ratio obtained with the two sets of zeolites are quite close at high Al content, at lower content the samples dealuminated by steam give more olefins than those dealuminated by $SiCl_4$.

It is clear that a model based only on the density of Brønsted sites cannot explain all the above results. To explain them, and since hydrogen transfer takes place by a series of consecutive reactions which involve readsorption of the olefins formed through primary and secondary cracking reactions, the first possibility we looked into was the textural characteristics of the samples. Indeed, the lower the restrictions for the products to diffuse out of the zeolite, the lower the hydrogen transfer should be. To check this possibility we give in Fig. 2 the surface area and the pore size distribution of the samples. In spite of the differences in the BET surface area, a more significant difference appears in the pore size distribution. It can be said that the mesoporosity (18–150 Å) in the steam-dealuminated samples is higher than that in the $SiCl_4$-

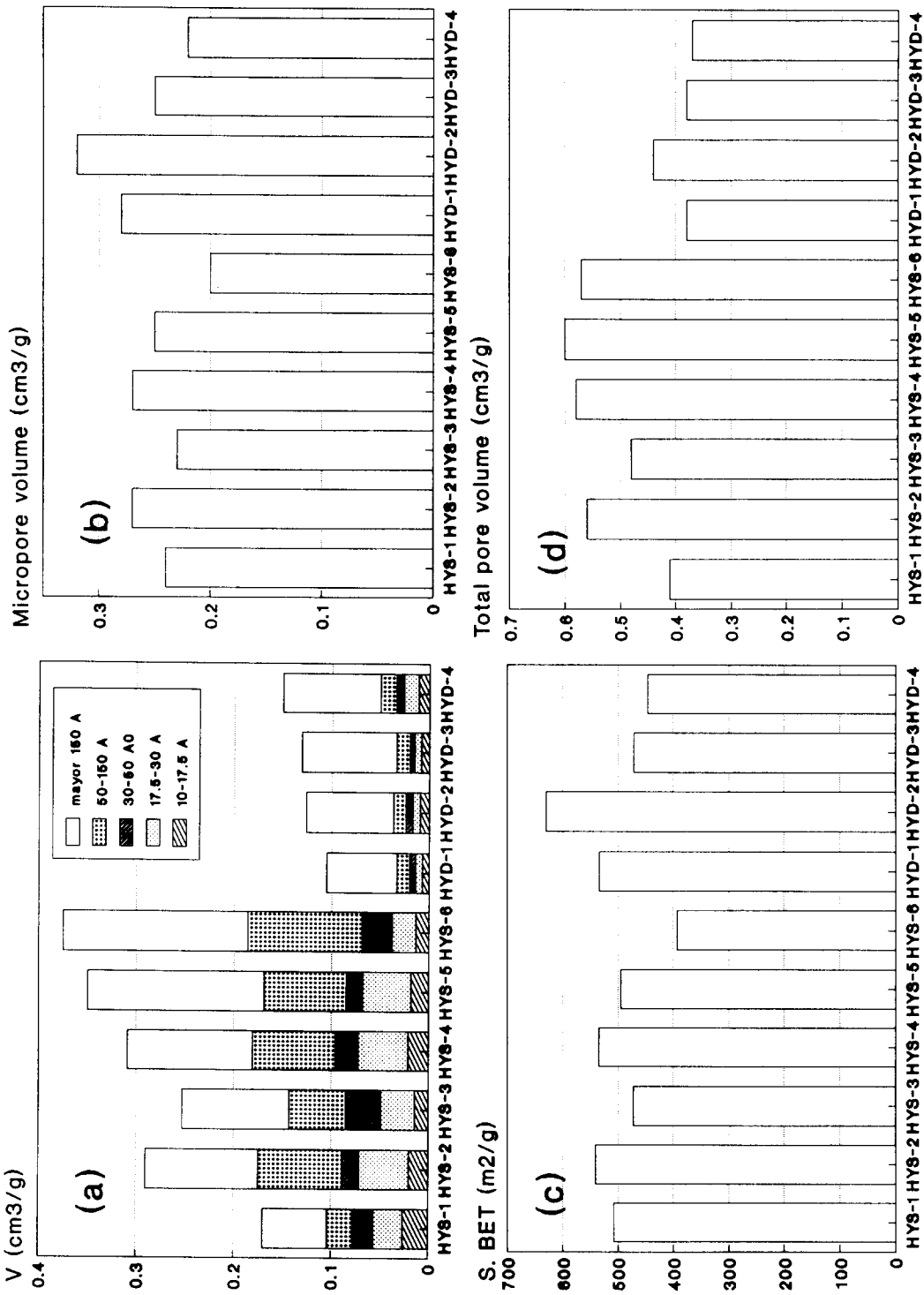

FIG. 2. (a) Pore size distribution of the samples. (b) Micropore volume. (c) BET surface area. (d) Total pore volume.

dealuminated samples. These results could, in principle, explain why hydrogen transfer is more extensive in $SiCl_4$-highly dealuminated than in the steam-dealuminated samples. Nevertheless, they cannot explain that similar hydrogen transfer values were obtained for the two sets of samples in the range of 30 to 15 Al per unit cell, even though large differences in pore size distribution were observed between them in that range of Si/Al ratios. Moreover, the mesoporosity of the steamed samples continuously and regularly increases with dealumination, while hydrogen transfer decreases only when the Al content is lower than 15 Al per unit cell. Similar reasoning can be applied to the results obtained with the $SiCl_4$-treated samples. Indeed, both samples, HYD-1 and HYD-4, give nearly the same butene/butane ratio, despite the fact that the mesoporosity of HYD-4 is more than 50% higher than that of HYD-1.

In conclusion, it becomes apparent that although the presence of mesoporosity in zeolites may have a beneficial effect in diminishing hydrogen transfer and, therefore, in increasing the olefinicity of the gasoline, there are other factors which contribute to the catalytic results presented in Fig. 1.

Other factors which may largely influence bimolecular and unimolecular competing reactions are possible differences in the adsorption capacity and the adsorption selectivity for hydrocarbons in dealuminated HY zeolites. The influence of the adsorption capacity on hydrogen transfer, and in general on bimolecular reactions, can be easily envisaged. More specifically, it was noted (*8*) that when amorphous silica–alumina was substituted for zeolites in catalytic cracking, besides the well-known effects on conversion and gasoline selectivity, the olefinicity of the gasoline decreased. This was explained by means of an increase in the rate of the hydrogen transfer reactions, as a consequence of the concentration of reactants inside the pores of the zeolite. Obviously, if dealumination decreases the concentration of reactants inside the pores of the zeolite, the rate of bimolecular reactions (hydrogen transfer) will decrease proportionally more than the rate of unimolecular (cracking) reactions. Moreover, if dealumination produces changes in the relative adsorption capacity for olefins and paraffins, these will clearly influence the relative rate of cracking to hydrogen transfer, since hydrogen transfer will necessarily need olefins to take place, while cracking of gas oil involves mainly alkanes, naphthenes, and alkyl aromatics.

Therefore, to check the influence of the level of dealumination on the adsorption characteristics of dealuminated HY zeolites we have carried out adsorption studies with two short-chain hydrocarbons, one olefin (1-butene) and one paraffin (1-butane), which do not present diffusion restrictions. Then, the qualitative and quantitative differences observed in adsorption were related to the catalytic results shown in Fig. 1.

Adsorption isotherms for 1-butene and *n*-butane are given in Figure 3. They show type I behavior in the BET classification, which is quite common for the adsorption of hydrocarbons on dealuminated zeolites (*17*). This is characteristic of chemisorption or physical adsorption in microporous solids. When increasing the adsorption temperature the isotherms drift away from the *y* axis, the effect being more notorious when the level of dealumination increases, which indicates that the interaction between the sorbate molecules and the bulk becomes smaller. The coverages decrease as expected with temperature (Table 2) and with the degree of dealumination (Figs. 3 and 4 and Table 3). The void space calculated decreases with increasing adsorption temperature and increasing level of dealumination (Table 3).

From Fig. 4, it can be seen that in the case of zeolites dealuminated by steam, the amount of *n*-butane and 1-butene adsorbed per unit surface area of the zeolite decreases as the number of Al per unit cell decreases, the decrease being much

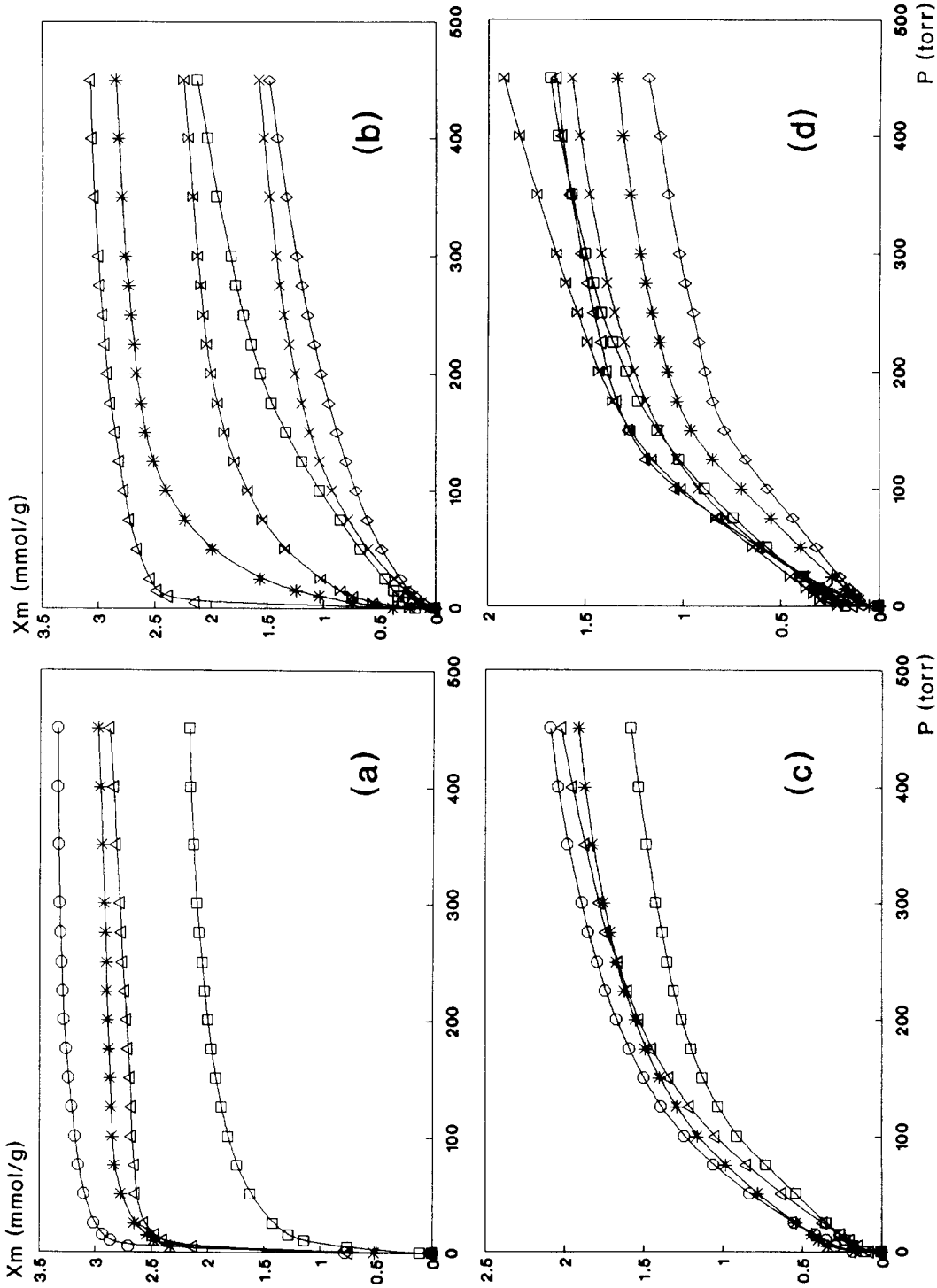

FIG. 3. Adsorption isotherms at 353 K on HYS and HYD zeolites. (a) 1-Butene on HYD: HYD-1 (△), HYD-2 (○), HYD-3 (*), and HYD-4 (□). (b) 1-Butene on HYS: HYS-1 (△), HYS-2 (*), HYS-3 (⊠), HYS-4 (×), HYS-5 (□), and HYS-6 (◇). (c) *n*-Butane on HYD. (d) *n*-Butane on HYS.

TABLE 2

Temperature Effects for the Adsorption of *n*-Butane and 1-Butene on HYS–HYD Zeolites

	X_m (mmol g^{-1})[a]							
	296 K		323 K		353 K		393 K	
	1-Butene	*n*-Butane	1-Butene	*n*-Butane	1-Butene	*n*-Butane	1-Butene	*n*-Butane
HYS-1	3.039	1.514	3.110	1.531	2.860	1.393	2.602	0.809
HYS-2	—	—	—	—	2.660	1.416	—	—
HYS-3	2.370	1.552	2.085	1.342	1.978	1.084	1.640	0.593
HYS-4	2.602	1.497	1.782	1.256	1.337	1.153	0.962	0.525
HYS-5	—	—	—	—	1.560	1.297	—	—
HYS-6	1.408	1.256	1.301	1.204	1.141	0.895	0.855	0.413
HYD-1	3.030	2.099	3.155	1.955	2.727	1.566	3.163	0.903
HYD-2	—	—	—	—	3.280	1.670	—	—
HYD-3	—	—	—	—	2.885	1.560	—	—
HYD-4	2.602	1.557	2.335	1.454	2.014	1.273	1.836	0.774

[a] Coverage, X_m, was calculated in mmol g^{-1} at 200 Torr.

stronger in samples with fewer than 10 Al/UC. This behavior is observed for all hydrocarbon partial pressures considered. The decrease is especially notorious for 1-butene, and much smaller for *n*-butane. In other words, dealumination not only produces a decrease in the capacity of adsorption, but also, at high levels of dealumination (typical range of FCC catalysts based on ultrastable zeolites), produces a decrease in the adsorption selectivity for olefins in comparison with paraffins. This can be better seen in Fig. 5.

The changes in adsorption can explain the catalytic results of Fig. 1. Indeed, in zeolites dealuminated by steam a small increase in the 1-butene/*n*-butane ratio obtained by adsorption is observed up to 10 Al/UC. If dealumination proceeds further, the butene/butane adsorption ratio strongly decreases, especially due to the decrease in the adsorption of 1-butene. At the same

TABLE 3

Parameters from the Isotherms of Adsorption of 1-Butene and *n*-Butane at 353 K

Sample	HYS-1		HYS-2		HYS-3		HYS-4		HYS-5		HYS-6	
	X_m[a] (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})
1-Butene	0.1638	0.28	0.1492	0.25	0.1122	0.20	0.0701	0.12	0.0875	0.15	0.0572	0.13
n-Butane	0.0805	0.15	0.0756	0.14	0.0628	0.12	0.0663	0.11	0.0831	0.13	0.0517	0.10

	HYD-1		HYD-2		HYD-3		HYD-4	
	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})	X_m (g g^{-1})	Void space (cm^3 g^{-1})
1-Butene	0.1526	0.27	0.1829	0.31	0.1619	0.27	0.1122	0.20
n-Butane	0.0886	0.17	0.0971	0.17	0.0907	0.16	0.0732	0.14

[a] Saturation uptake, X_m, was calculated in g g^{-1} of zeolite at p = 200 Torr.

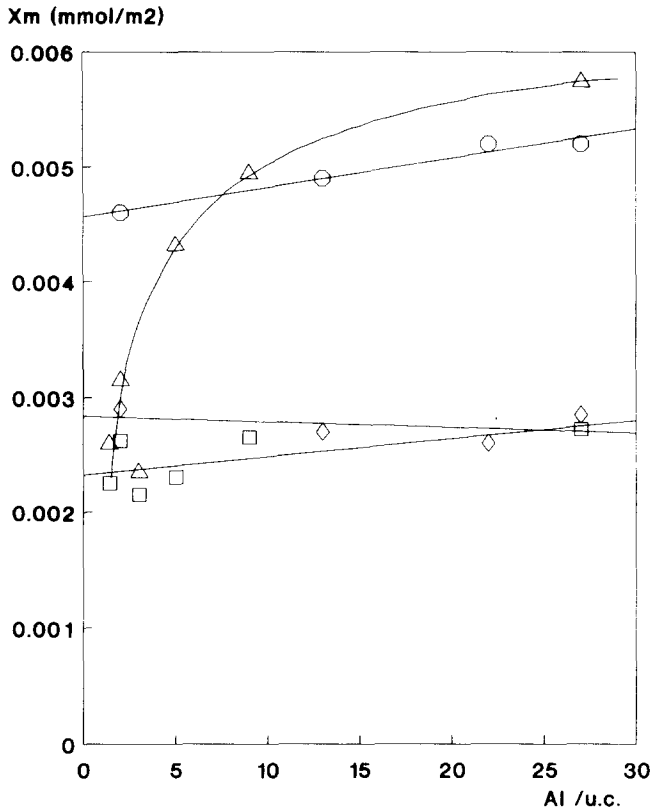

FIG. 4. Variation of adsorption coverages per unit surface area with the number of Al atoms per unit cell (calculated at 200 Torr at 353 K). (△) 1-Butene on HYS, (○) 1-butene on HYD, (□) *n*-butane on HYS, and (◇) on HYS zeolites.

time the olefinicity of the gasoline, measured from the butene/butane ratio obtained during cracking of gas oil, changes very little up to ≈15 Al/UC, and then strongly increases. It seems, therefore, that a decrease in the adsorption of olefins, which is a necessary step in the bimolecular hydrogen transfer reactions, will produce a strong decrease in the rate of olefin saturation. On the other hand, the rate of cracking of the gas oil, which is composed mainly of paraffins and cycloalkanes, will be less affected than hydrogen transfer by dealumination on the basis of the small changes observed in the adsorption of butane. Then, in steam-dealuminated zeolites, one should expect, the ratio of cracking to hydrogen transfer will increase in HY zeolites with fewer than 10 Al/UC, as is observed here and, indeed, in commercial FCC operations.

In the case of HY zeolites dealuminated by $SiCl_4$, it is seen in Fig. 4 that the amounts of *n*-butane and 1-butene adsorbed per unit surface area of the zeolite are practically the same for samples with 27 and 2 Al per unit cell; i.e., no differences in the relative adsorption of olefins and alkanes are observed. According to our hypothesis, only small changes should be observed in the relative rates of hydrogen transfer and cracking when comparing the four HYD samples. Indeed, the results from Fig. 1 clearly show that the hydrogen transfer obtained in the cracking of gas oil is practically the same. Moreover, if one compares the adsorption results of the steam- and $SiCl_4$-dealuminated samples (Fig. 4 and Ta-

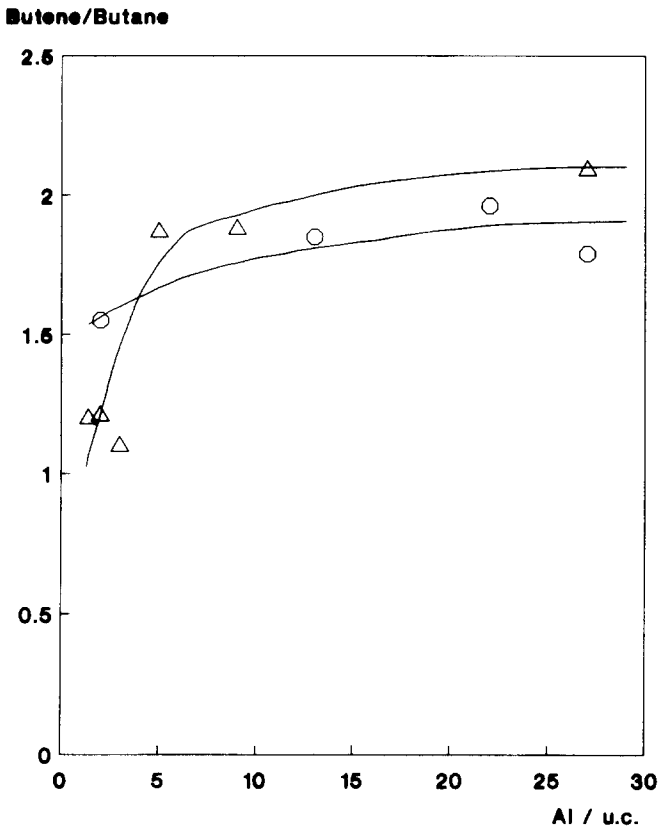

FIG. 5. Variation of butene/butane ratio with the number of Al atoms per unit cell, from adsorption on HYS (△) and HYD (○) zeolites at 353 K and 200 Torr.

ble 2), it is clear that the samples with 27 Al/UC content give nearly the same adsorption and hydrogen transfer results regardless of the method of dealumination. On the other hand, for highly dealuminated samples (UC = 24.25 Å), those dealuminated with $SiCl_4$ not only adsorb more *n*-butane and 1-butene (Fig. 4) but also show higher relative adsorption of olefins/alkanes (Fig. 5).

Following our hypothesis that the higher the adsorption capacity and the more selective the adsorption of olefins, the higher will be the hydrogen transfer catalytic activity of the HY zeolites, the results of Fig. 4 for C_4 adsorption would indicate that $SiCl_4$ should give more hydrogen transfer than steam-dealuminated samples. Indeed, the catalytic results from Fig. 1 support the above hypothesis.

CONCLUSIONS

Changes in adsorption capacity and adsorption selectivity on zeolites upon dealumination will change the relative rate of bimolecular (hydrogen transfer) to unimolecular (cracking) reactions and therefore the observed selectivities. In the case of HY zeolite, the adsorption characteristics, and therefore the hydrogen transfer-to-cracking ratio, depend not only on the framework Si/Al ratio but also on the procedure to dealumination. It can be said, therefore, that the differences in adsorption will be governed by the electric fields inside the zeolite, and therefore the presence of

adjacent Brønsted sites is not necessary to explain the hydrogen transfer to cracking selectivity.

Similar characteristics of the adsorption can be achieved, for instance, by combination of two close Brønsted sites or by combination of one Brønsted site and another type of cation.

ACKNOWLEDGMENT

Financial support by the Comision Asesora de Investigación Científica y Técnica of Spain (Project PA 85-0284) is gratefully acknowledged.

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