JOURNAL OF CATALYSIS **125**, 197–206 (1990)

Cracking of Light Alkanes over HNaK Erionites

ANDREAS KOGELBAUER AND JOHANNES A. LERCHER

Institut für Physikalische Chemie, Technische Universität Wien,
Getreidemarkt 9, A-1060 Vienna, Austria

Received December 5, 1989; revised March 6, 1990

The activity and selectivity of a series of partially exchanged HNaK erionites for cracking of *n*-butane and *n*-hexane were investigated. Only the strong Brønsted acid sites (Si–OH–Al groups) were concluded to be active. The turnover frequencies for both reactions increased proportionally to the positive charge at the proton of the strong Brønsted acidic OH group calculated according to the electronegativity model of Sanderson. The positive influence of the increasing charge of the protons (i.e., of their acid strength) is also evidenced in the decrease in the apparent energy of activation for the cracking reaction. The product selectivity suggests that the molecules are cracked according to the monomolecular mechanism. Dehydrogenation gains importance with increasing strength of the protons and decreasing reaction temperature.

INTRODUCTION

Cracking of hydrocarbons is a widely used experimental means to characterize acidic catalysts. A large variety of molecules has been used as reactants (*1–6*), each of which was claimed to have specific benefits for characterization. In general, however, saturated hydrocarbons with up to nine carbon atoms have been used to classify the strength and activity of acid catalysts or, better, of acid sites of catalysts (*4, 5, 7–12*), while cracking of significantly larger hydrocarbons has been applied to characterize the pore geometries of microporous solids (*13–15*).

All authors agree that Brønsted acid sites are indispensible for catalyzed cracking of hydrocarbons (*6, 16, 17*) and excellent reviews cover aspects of hydrocarbon protonation (*17–19*). Disagreement exists, however, whether or not the specific rate per site should depend upon the composition (and in consequence upon the strength of a particular catalytically active proton) and upon the concentration of acid sites.

Thus, communications concerning the variation of catalytic activities for conversion of hydrocarbons as a function of the chemical composition of the catalyst can be divided into two groups: (i) reports of varying activity per acidic proton and (ii) reports of equal activity per acidic proton.

Examples for the first case include the nonlinear dependence of the rate of the catalytic decomposition of neopentane, isobutane, and *n*-hexane over H-mordenite samples upon the aluminum concentrations of the zeolites used (*8*). Similarly, nonlinear relationships between the catalytic activity for cumene cracking or for isooctane cracking over NaHY were reported by Turkevich *et al.* (*20, 21*) and by Beaumont *et al.* (*22*), respectively.

The second case may be best illustrated by the constant turnover frequencies (TOF, i.e., the rates of cracking normalized to the concentration of the Brønsted acid sites) for cracking of *n*-hexane over pentasil zeolites irrespective of the aluminum content of the samples (*10, 23*). Similarly, Halik *et al.* (*24*) found constant turnover frequencies for *n*-butane and *n*-hexane cracking over SAPO5 samples with varying silicon content. Estimation of the TOFs for cracking of *n*-heptane and *n*-octane over NH_4^+-exchanged erionites according to data of Mirodatos and Barthomeuf (*9*) also showed constant TOF for samples with different degrees of cation exchange.

0021-9517/90 $3.00

The purpose of this paper is to describe the cracking of *n*-butane and *n*-hexane over a series of partially cation-exchanged HNaK erionites and to evaluate the influence of alkali cations upon the catalytic activity of strong Brønsted acid sites. We intend to show that the increase in catalytic activity for cracking of *n*-hexane and *n*-butane with increasing degree of NH_4^+ exchange is due to both an increase in the concentration of catalytically active sites and the specific activity per site. We will use IR spectroscopy and TPD of ammonia to show that it is an increase in acid strength which causes the increase in catalytic activity per proton. All catalytic reactions were performed under experimental conditions which cause the proton transfer to the saturated hydrocarbon to be rate determining. Thus, the specific rate and the energies of activation of the reaction should reflect the strength of the proton catalyzing the cracking reaction.

EXPERIMENTAL

Zeolites

The erionite sample was obtained from VEB Chemiekombinat Bitterfeld, GDR. The parent Na,K-erionite was repeatedly ion exchanged with NH_4NO_3 solution at 363 K and dried at 370 K. Samples with high degrees of NH_4^+ exchange were intermediately calcined at 770 K as described previously (*25*). The unit cell compositions and the concentration of Brønsted acid sites of partially NH_4^+-exchanged erionite are compiled in Table 1.

IR Measurements

The samples were pressed into self-supporting wafers and analyzed by means of the transmission–absorption technique. The instrument used was a BRUKER IFS88 FTIR spectrometer. For each spectrum 150 interferograms were coadded. The spectral resolution was 4 cm^{-1}. The IR cell used allowed all investigations (heating, adsorption) to be performed with the zeolite wafer present in the IR beam. The samples were activated for 1 h at 770 K at pressures below 10^{-6} mbar. After cooling to 308 K the samples were subsequently equilibrated with *n*-hexane at constant partial pressures, starting with 10^{-5} mbar up to 10 mbar.

Catalytic Measurements

Cracking of *n*-butane and *n*-hexane were carried out in a quartz glass tube reactor 300 mm in length and with an inner diameter of 4 mm. In order to avoid channeling, a minimum catalyst bed length of 10 mm was used. The reactor effluent was sampled at appropriate time intervals by means of a six-port valve. A HP 5890 gas chromatograph, equipped with a 50-m-long Al_2O_3–KCl-coated capillary column and a FID was used for analysis. The feeds contained 2 mol% *n*-butane and 14.7 mol% *n*-hexane, respectively. Before reaction, the samples were activated for 1 h at 770 K in flowing

TABLE 1

Unit Cell Composition of Partially Exchanged Erionite

Sample	Exchange (% NH_4)	Brønsted acid sites (mol/g)	Stoichiometric quantities				
			NH_4	K	Na	AlO_2	SiO_2
0.35 HERIO	35	4.29×10^{-4}	3.14	4.29	1.57	9	27
0.47 HERIO	47	7.86×10^{-4}	4.26	3.82	0.92	9	27
0.75 HERIO	75	1.52×10^{-3}	6.72	2.06	0.22	9	27
0.88 HERIO	88	1.92×10^{-3}	7.94	1.01	0.05	9	27
0.92 HERIO	92	2.00×10^{-3}	8.28	0.69	0.02	9	27

He. All measurements reported refer to activity and selectivity at steady state, which was usually reached after 30 min on stream. The samples that showed significant loss of activity with time on stream were regenerated with air and purged with helium before the temperature was changed. The conversion was kept below 5% by adjusting the amounts of catalyst used and the flow rates. The data were analyzed according to the differential method (*26*).

Thermogravimetric Measurements

The concentration of adsorbed *n*-hexane was determined by means of a CAHN RG microbalance. The system could be evacuated below 10^{-5} mbar. Adsorption isotherms were measured at 308 K after equilibration at 373 K. This procedure was found to be necessary to achieve complete saturation.

RESULTS

Adsorption of n-Hexane

The activated zeolites exhibited bands of OH stretching vibrations at 3741, 3691, 3618–3608, and 3566 cm^{-1}, which were attributed to silanol groups terminating the lattice (3741 cm^{-1}), water adsorbed on sodium cations (3691 cm^{-1}), strong Brønsted acid sites located in the supercages (3618–3608 cm^{-1}), and hydroxyl groups located in the cancrinite cages (3566 cm^{-1}) (*25*). After adsorption of *n*-hexane on the activated samples at 300 K three bands at 2952, 2929, and 2864 cm^{-1} were observed in the region of CH stretching vibrations and two bands at 1462 and 1380 cm^{-1} in the region of CH deformation vibrations. The wavenumbers of the bands of the CH vibrations did not change as a function of the partial pressure. The band at 3608–3618 cm^{-1}, which is attributed to strong Brønsted acid sites (*25*), showed a significant decrease in intensity upon *n*-hexane adsorption. In parallel, the band at 3566 cm^{-1}, attributed to Si–OH–Al hydroxyl groups located in cancrinite cages, was only modestly affected.

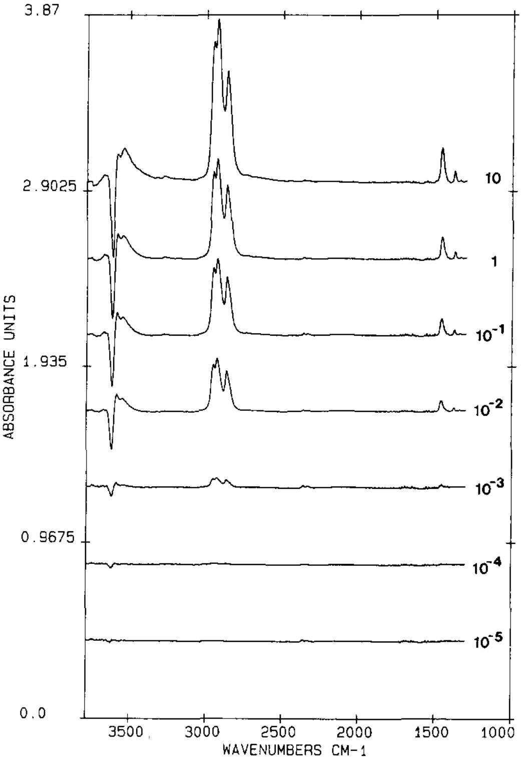

FIG. 1. Difference between the IR spectra of 0.75 HERIO equilibrated with *n*-hexane at pressures indicated (mbar) and the IR spectrum of the activated sample at ambient temperature.

As an example, Fig. 1 shows the difference between the IR spectra of the sample 0.75 HERIO equilibrated with *n*-hexane at the partial pressures indicated and the spectrum of the activated sample. In this graph bands pointing downward indicate the decrease in intensity, bands pointing upward indicate an increase in intensity of an IR band in comparison to the reference spectrum. With increasing equilibrium pressure the intensity of the bands of CH vibrations increased, indicating increasing amounts of adsorbed *n*-hexane. After equilibration with pressures below 10^{-2} mbar, only the band of the strong Brønsted acid sites (3608–3618 cm^{-1}) decreased in intensity (which causes an increase in intensity in the negative band at 3610 cm^{-1} in the difference plot), indicating, thus, a decrease in the concentration of the unperturbed Si–OH–Al groups. The band between 3540–3550 cm^{-1} is attributed to Si–OH–Al groups (strong Brønsted acid sites) interacting with *n*-hexane. The wavenumber of this band shifted to lower wavenumbers with increasing equilibrium pressure. The difference between this wavenumber and that of the unperturbed Si–OH–Al groups increased from 27 cm^{-1} at 10^{-5} mbar to 76 cm^{-1} at 10 mbar, indicating increasing intensity of the perturbation with increasing equilibrium pressure.

At equilibrium pressures higher than 10^{-1} mbar the terminal silanol groups (3741 cm^{-1}) and the hydroxyl groups due to water adsorbed on sodium cations (3691 cm^{-1}) (*27*, *28*) also interacted with *n*-hexane.

The small (negative) band at 3558 cm^{-1} in Fig. 1 indicates that at least some weak interaction between the hardly accessible Brønsted acid OH groups located in the cancrinite cages and the hexane molecules occurred. Note that in comparison to the strong Brønsted acid sites located in the supercage, only a small fraction of these acid sites interacted with *n*-hexane.

Considering the molecular dimensions of the *n*-hexane molecule (3.9 × 4.3 Å (*29*)) and the diameter of the six-ring windows of the cancrinite cage (2.5 Å), adsorption should not occur at all on these sites (i.e., Si–OH–Al groups located inside the cancrinite cages). Three explanations of the experimentally observed adsorption might then be possible: (i) some of the Si–OH–Al groups are located close to the six-ring windows and have a limited accessibility for *n*-hexane; (ii) the six-ring windows show high flexibility, especially in combination with a small concentration of lattice defect sites (and thus allow part of the *n*-hexane molecule to enter the cancrinite cage); and (iii) the protons are relatively mobile and migrate into the more accessible pore system.

After equilibrating the erionite samples with *n*-hexane at the same partial pressure (10 mbar) the shift of the band of the strong Brønsted acid hydroxyl groups to lower wavenumbers increased with increasing concentration of strong Brønsted acid sites, from 30 cm^{-1} for 0.35 HERIO to 96 cm^{-1} for 0.88 HERIO. In accordance with Hair and Hertl (*30*), this was attributed to an increasing acid strength of the considered protons, which agrees well with previous TPD experiments (*25*).

Cracking of n-Butane and n-Hexane

The turnover frequencies for cracking of *n*-butane and *n*-hexane over erionite samples at 753 K and the apparent energies of activation are compiled in Table 2. All rates were measured under steady-state conditions between 673 and 753 K. For the calculation of the TOF the C_4 (*n*-butane cracking) or C_6 (*n*-hexane cracking) products were not considered, because they originate from dehydration and/or isomerization reactions. The selectivity of the samples to cracking products at 753 K is shown in Figs. 2 and 3. With increasing degree of NH_4^+ exchange of the erionite samples, the TOF increased drastically. While the concentration of Brønsted acid sites increased five times from 0.35 to 0.92 HERIO, the rate per site increased by nearly two orders of magnitude. In the sequence in which the turnover frequencies increased, the apparent energies of activation decreased.

TABLE 2

Specific Cracking Activity and Apparent Energy of Activation of Partially Exchanged Erionite

Sample	*n*-Butane		*n*-Hexane	
	TOF (753 K) (s^{-1})	E_a (kJ/mol)	TOF (753 K) (s^{-1})	E_a (kJ/mol)
0.35 HERIO	1.0×10^{-6}	151	5.5×10^{-5}	171
0.47 HERIO	4.0×10^{-6}	144	3.5×10^{-4}	162
0.75 HERIO	3.2×10^{-5}	136	5.0×10^{-3}	135
0.88 HERIO	6.0×10^{-5}	121	9.5×10^{-3}	113
0.92 HERIO	7.0×10^{-5}	115	1.0×10^{-2}	105

Note. Accuracy of data: TOFs ±3%, E_a ±5%.

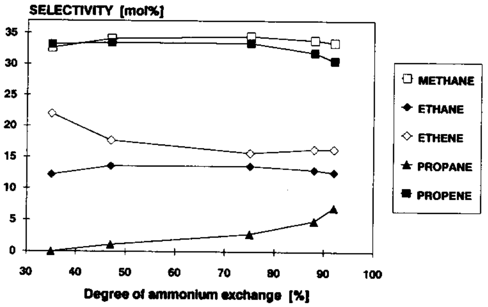

FIG. 2. Product selectivity for *n*-butane cracking over partially NH_4^+-exchanged erionites at 753 K.

DISCUSSION

Adsorption of n-Hexane

IR spectroscopic investigations of *n*-hexane adsorbed on the erionite samples indicate that at low equilibrium pressures primarily the bridging hydroxyl groups (with bands at 3608–3618 cm^{-1}) are involved in the adsorption process. These hydroxyl groups are located in the main channels (*25*). Because of the minute changes in intensity of the band at 3566 cm^{-1}, only a minute fraction of the bridging hydroxyl groups in the cancrinite cages are concluded to interact with *n*-hexane at 300 K. We suggest that this fraction of Si–OH–Al groups is located close to the six-ring windows. Our proposal is based on the fact that ammonia is chemisorbed on all strong Brønsted acid sites located in the cancrinite cages, while molecules like propene and hexane only interact with a small fraction of these sites. We think that the strong base ammonia also attracts the protons of the Si–OH–Al groups further apart from the six-ring window into the supercage and forms NH_4^+ ions, while the weaker basic propene (*31*) and *n*-hexane may only affect the sites close to the six-ring windows.

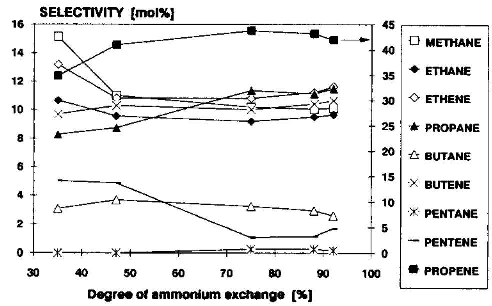

FIG. 3. Product selectivity for *n*-hexane cracking over partially NH_4^+-exchanged erionites at 753 K.

The difference in wavenumber of the OH stretching vibration of the free Si–OH–Al groups and of those interacting with *n*-hexane is extremely small compared with those of zeolites like HZSM5. For HZSM5 Jentys *et al.* (*32*) observed a shift in the OH band of 125–160 cm^{-1} on adsorption of *n*-hexane. In part, this is attributed to the higher acid strength of HZSM5 in comparison with that of the erionite samples investigated in this paper. The shifts observed for the samples with a low degree of NH_4^+ exchange are, however, so small that steric constraints hindering the interaction between the Si–OH–Al groups and the *n*-hexane molecule must also be considered. The higher molar extinction coefficient of the band of the perturbed OH groups on HZSM5 and even on SiO_2 supports this latter argument.

Nevertheless, the increase in the shift as a function of the degree of NH_4^+ exchange suggests increasing acid strength of the Si–OH–Al groups (*30*). Figure 4 shows this

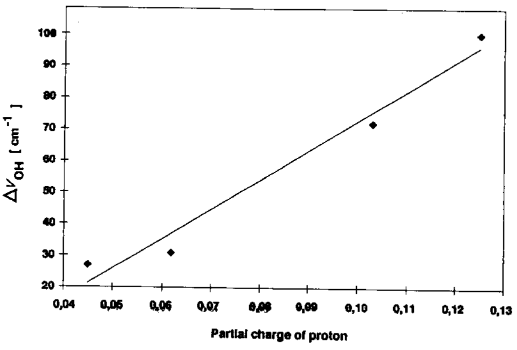

FIG. 4. Difference in wavenumbers between the bands of the bridged hydroxyl groups prior to and after equilibration with *n*-hexane at 10 mbar and ambient temperature as a function of the partial charge of the proton calculated according to Sanderson.

shift of the band of the Si–OH–Al group as a function of the partial charge of the proton. The plot indicates that the strength of the acid sites is directly proportional to the positive charge estimated by means of Sanderson's electronegativity (*33*).

For a given sample, an increase in that shift was also observed with increasing equilibrium pressure (coverage), pointing to stronger perturbations of the Si–OH–Al groups by the adsorbed molecules as the coverage rises. Gravimetric results suggest that at low equilibrium pressures, one *n*-hexane molecule per supercage was adsorbed. Because the IR experiments suggest that all Si–OH–Al groups in the supercage (two to three) interact with the *n*-hexane molecule simultaneously, it may be quasi-suspended in the supercage. At higher concentrations of *n*-hexane in the pores a second molecule may be adsorbed per supercage, causing closer packing, which in turn allows each of the two molecules to interact more strongly with the Brønsted acid sites at the walls of the supercage. Because of the adsorption stoichiometry per site and the constraint space in the pores, multiple adsorption of *n*-hexane on one site can be ruled out as a cause for that increase in the strength of interaction between the hydroxyl groups and the *n*-hexane molecules.

Catalytic Activity for Cracking of n-Alkanes

The catalytic activity for cracking of *n*-hexane and *n*-butane increased with increasing degree of ammonium exchange. In general, such an observation might be explained either by an increase in the concentration of the catalytic active sites, by an increase in the activity per active site, or by a combination of both. The importance of the increase of the concentration of acid sites was accounted for by normalizing the rate to the concentration of acid sites (i.e., by using the turnover frequencies). Figure 5 shows the increase in the TOF for cracking of *n*-hexane and *n*-butane at 753 K with increasing degree of NH_4^+ exchange of the erionite samples. Two reasons for the observed increase are conceivable: (i) an increase in the strength of the protons with increasing degree of ion exchange and (ii) an increase in the rate due to a higher surface concentration, especially under conditions favoring a bimolecular mechanism for cracking (*34*), i.e., at lower temperatures and higher alkane partial pressures. In order to minimize the effects of higher surface concentrations of the reactants, cracking of both *n*-hexane and *n*-butane was performed under reaction conditions favoring a monomolecular mechanism of cracking (*34*). Thus, the protonization of the saturated hydrocarbon should be the rate-determining step (*17, 34*). It is then to be expected that the reaction per site should be faster the stronger the acidic site is. Thus, we attribute the increase in TOF to an increase in acid strength with increasing degree of NH_4^+ exchange.

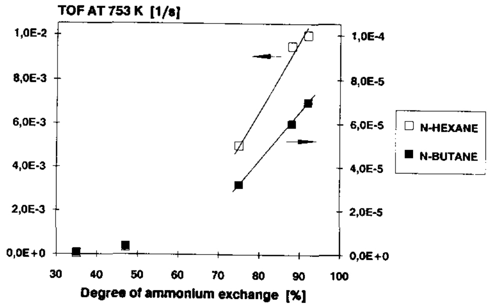

FIG. 5. Turnover frequencies for *n*-hexane cracking and *n*-butane cracking over partially NH_4^+-exchanged erionites at 753 K as a function of the degree of NH_4^+-exchange.

Four additional observations also suggest that the acid strength of the protons increases with increasing degree of NH_4^+ exchange. First, as discussed above, the difference in wavenumbers between the band of unperturbed Brønsted acidic hydroxyl groups located in the supercages and the band of these hydroxyl groups interacting with *n*-hexane suggests increasing acid strength of the Brønsted acidic hydroxyl

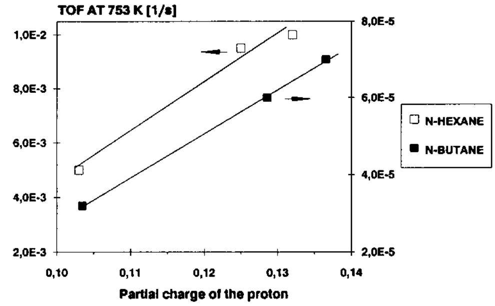

FIG. 6. Turnover frequencies for *n*-hexane cracking and *n*-butane cracking over partially NH_4^+-exchanged erionites at 753 K as a function of the partial charge of the proton calculated according to Sanderson.

groups with increasing degree of NH_4^+ exchange. Second, Dyer and Singh (*35*) reported a more distinct effect on the catalytic activity for *n*-butane cracking on mordenites after poisoning by potassium than by sodium. In the absence of transport limitations (which could be imposed by the larger potassium ion), this clearly suggests an overall influence of the exchangeable cation upon the strength of the proton. Third, one notes a direct proportionality between the positive charge and the TOF for *n*-hexane and *n*-butane cracking for the samples with more than 50% of all potential acidic sites being protons (see Fig. 6). And last, the decreasing apparent energy of activation suggests increasing facility to protonate the alkane molecules. It should be mentioned, however, that the last of these effects may also be explained by variations in the heat of adsorption of the *n*-alkane molecule, as pointed out by Haag *et al.* (*36*).

An important argument against the inherent nonlinear variation in the catalytic activity with the chemical composition of molecular sieves is the likely existence of sites of extremely high activity generally caused by mild steaming conditions (*37, 38*). It may be argued that these sites may only (or in an increasing concentration) exist under conditions of high NH_4^+ exchange (*39*). As an example, Fritz and Lunsford (*40*) discussed the poisoning effect of sodium on Y-type zeolites. The exchange of protons for sodium led to a dramatic decrease in the catalytic activity for *n*-hexane cracking. They concluded that only about one-fifth of the framework aluminum was associated with sites revealing extremely strong Brønsted acidity. They related this high acid strength ("super acid sites") to the presence of extra lattice aluminum in the vincinity of a briding OH group.

While we cannot exclude such an effect completely, we do not think that it solely contributes to the observed increase in the TOF. The main argument against it is the linear dependence of the TOF with the increase in the partial charge of the proton. In order to explain this increase by an increase in concentration of the "super acid sites," one must assume a linear increase in the concentration of the "super acid sites" with increasing average charge of the proton. This is not very probable.

In general, we do not think that the discrepancies concerning the catalytic activity of partially exchanged erionites noted in the Introduction can be related to subtle differences in the heat of adsorption of reactant molecules or in the concentration of very strong Brønsted acid sites generated by varying pretreatment procedures. It may rather be suggested to be due to the leveling effect of coking as indicated by Mirodatos and Barthomeuf (*9*).

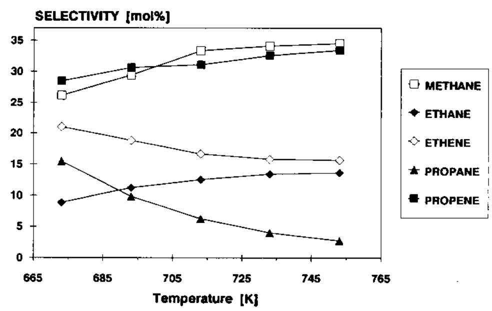

FIG. 7. Product selectivity for *n*-butane cracking over 0.75 HERIO as a function of the reaction temperature.

In this paper the calculated TOFs for cracking of paraffins over partially exchanged erionites after 2 and 15 h on stream were constant, whereas those calculated for the initial activities (after 3 min on stream) were not. Thus, for catalysts after a long time on stream, the higher activity of the samples with a higher degree of ion exchange might be overcompensated for by a higher coke level caused by a faster rate of coking. This explanation is strongly supported by other data of Mirodatos and Barthomeuf (*41*) which indicate a nonlinear relationship between catalytic activity for cracking of *n*-paraffins and degree of ion exchange after a short time on stream.

Selectivity to Cracking Products

Figure 2 shows that the methane/propene ratios for conversion of *n*-butane at 753 K over all samples investigated lie near 1. That implies that both products result only from a primary cracking step. It is not possible to conclude unequivocally whether they are formed via a protolytic mechanism (α-scission) or via a carbenium ion (β-scission).

If the scission took place in the β position to the carbon atom bearing the positive charge, it is unlikely that a large fraction of *n*-butane molecules would be cracked to C_2 fragments. Thus, the major fraction of C_2 products is concluded to result from a monomolecular (protolytic) process. Because the concentration of ethene was somewhat higher than the concentration of ethane and butene was detected in the reaction products (between 14 and 16 mol% of the products for all samples and slightly increasing with temperature), we concluded that to some extent dehydrogenation took place simultaneously with cracking. This also supports our view that cracking proceeds primarily via the monomolecular mechanism under our conditions.

The fraction of ethane formed over a specific zeolite sample increased with increasing reaction temperature (see Fig. 7). Because we have attributed the higher concentration of ethene to be caused by dehydrogenation of butane prior to cracking, the increase in ethane in the products suggests that dehydrogenation and/or initiation via hydride abstraction decreases in importance as the reaction temperature increases.

The presence of propane (which decreases in concentration with increasing reaction temperature) cannot be explained without the presence of another parallel process. We propose that propane is formed through hydride transfer to the propyl carbenium ion. Sources for the hydride ion should be strongly adsorbed hydrocarbons or coke precursors. In this context, Abbot and Wojciechowski (*42, 43*) reported that initial paraffin/olefin ratios greater than 1 indicate hydrogen transfer from coke precursors to carbenium ions. The role of strongly adsorbed hydrocarbons or coke precursors as a source of hydride ions is also indicated from the moderate increase in propane selectivity at 753 K with increasing degree of NH_4^+ exchange, i.e., with increasing acid strength. In parallel, the overall paraffin/olefin ratio of the reaction products increased from 0.60 for 0.35 HERIO to 0.82 for 0.92 HERIO. Following the concept of Lombardo *et al.* (*6*), the increase in the paraffin/olefin ratio reflects the stability of a carbenium ion on the surface of the solid acid. The more stable it is (i.e., the more acidic the hydroxyl group are) the higher is the probability that secondary reactions like hydrogen transfer, oligomerization, etc., take place. Because of the C_3/C_1 ratio of 1.7 at lower temperatures, we concluded that some oligomerization must have taken place over samples with more then 70% NH_4^+ exchange. Note that his ratio decreased as the reaction temperature was raised.

For *n*-hexane cracking the same conclusions as those for the cracking of *n*-butane are valid. In accordance with other reports, C_3 compounds were found to be the main reaction product (*16, 44, 45*). To a smaller extent C_4 plus C_2 products also occur due to β-scission of a carbenium ion with the positive charge located on the third carbon atom. The relatively high selectivity to methane and ethane again supports the predominance of the monomolecular, protolytic cracking mechanism (*46*). C_5 compounds could be observed only in minor concentrations, which indicates that the C_5 carbenium ion likely undergoes secondary reactions.

The increased methane production with the less acidic samples is concluded to be caused by secondary cracking reactions because the space velocity during the catalytic runs over these catalysts was rather low compared to that of the other samples. The pronounced selectivity to propene was concluded to be due to dehydrogenation or hydride abstraction preceding the cracking reaction. Indeed, significant selectivities to hexene were observed, although the molecule is easily cracked under the conditions employed.

CONCLUSIONS

Cracking of *n*-butane and *n*-hexane over a series of partially exchanged HNaK erionites revealed a strong dependence of the rate and the apparent energy of activation upon the chemical composition of the catalyst. Under reaction conditions favoring the monomolecular mechanism of cracking, only the strong Brønsted acid sites (Si–OH–Al groups) were thought to be active. The rate of cracking was found to be directly proportional to the charge at the proton calculated according to Sanderson (*33*). Several independent measurements (*9, 25, 41*) also suggest an increase in the acid strength of the protons of Si–OH–Al groups with the degree of NH_4^+ exchange. Thus we propose that the increase in the rate is due to the easier protonization of the saturated hydrocarbon molecule. This is in agreement with the fact that protonization of the alkane is the rate determining step in a monomolecular pathway of cracking and is also supported by the decreasing apparent energies of activation with the degree of NH_4^+ exchange.

ACKNOWLEDGMENT

This work was supported by the Jubiläumsfonds der Österreichischen Nationalbank under Contract 4360.

REFERENCES

1. Bizreh, Y. W., and Gates, B. C., *J. Catal.* **88,** 240 (1984).

2. McVicker, G. B., Kramer, G. M., and Ziemiak, J. J., *J. Catal.* **83,** 286 (1983).

3. Chen, N. Y., and Garwood, W. E., *J. Catal.* **52,** 453 (1978).

4. Weisz, P. B., and Miale, J. N., *J. Catal.* **4,** 527 (1965).

5. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966).

6. Lombardo, E. A., Pierantozzi, R., and Hall, W. K., *J. Catal.* **110,** 171 (1988).

7. Rastelli, H., Jr., Lok, B. M., Duisman, J. A., Earls, D. E., and Mullhaupt, J. T., *Canad. J. Chem. Eng.* **60,** 44 (1981).

8. Lombardo, E. A., Gaffney, T. R., and Hall, W. K., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 1, p. 412, Institute of Canada, Ottawa, 1988.

9. Mirodatos, C., and Barthomeuf, D., *J. Catal.* **93,** 246 (1985).

10. Olson, D. H., Haag, W. O., and Lago, R. M., *J. Catal.* **61,** 390 (1980).

11. Corma, A., Monton, J. B., and Orchilles, A. V., *Appl. Catal.* **16,** 59 (1985).

12. Frilette, V. J., Haag, W. O., and Lago, R. M., *J. Catal.* **67,** 218 (1981).

13. Martens, J. A., and Jacobs, P. A., *Zeolites* **6**(5), 334 (1986).

14. Martens, J. A., Tielen, M., Jacobs, P. A., and Weitkamp, J., *Zeolites* **4**(2), 98 (1984).

15. Jacobs, P. A., and Martens, J. A., *Stud. Surf. Sci. Catal.* **28,** 23 (1986).

16. Greensfelder, B. S., Voge, H. H., and Good, G. M., *Ind. Eng. Chem.* **41,** 2573 (1949).

17. Wojciechowski, B. W., and Corma, A., "Catalytic Cracking, Catalysts, Chemistry, and Kinetics," p. 6. Dekker, New York, 1986.

18. Corma, A., Planelles, J., Sanchez-Marin, J., and Tomas, F., *J. Catal.* **93,** 30 (1985).

19. Planelles, J., Sanchez-Marin, J., Tomas, F., and Corma, A., *J. Mol. Catal.* **32,** 365 (1985).

20. Turkevich, J., Murakami, Y., Nozaki, F., and Ciborowski, S., *Kinet. Catal. Chem. Eng. Prog., Symp. Ser. 73,* **63,** 75 (1967).

21. Turkevich, J., Nozaki, F., and Stamires, D., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," Vol. 1., p. 587. North-Holland, Amsterdam, 1965.

22. Beaumont, R., Barthomeuf, D., and Trambouze, Y., *Adv. Chem. Ser.* **102,** 327 (1971).

23. Dwyer, J., Fitch, F. R., and Nkang, E. E., *J. Phys. Chem.* **87,** 5402 (1983).
24. Halik, C., Chaudhuri, S. N., and Lercher, J. A., *J. Chem. Soc. Faraday Trans. 1* **85**(11), 3879 (1989).
25. Kogelbauer, A., Lercher, J. A., Steinberg, K. H., Roessner, F., Soellner, A., and Dmitriev, R. V., *Zeolites* **9**(3), 224 (1989).
26. Swinbourne, E. S., "Analysis of Kinetic Data," p. 78. Nelson, London, 1971.
27. Hair, M. L., "Infrared Spectroscopy in Surface Chemistry," p. 183. Dekker, New York, 1967.
28. Ward, J. W., "Zeolite Chemistry and Catalysis," p. 187. Amer. Chem. Soc., Washington, DC, 1976.
29. Chen, N. Y., Garwood, W. E., and Dwyer, F. G., "Shape-Selective Catalysis in Industrial Applications," p. 10. Dekker, New York, 1989.
30. Hair, M. L., and Hertl, W., *J. Phys. Chem.* **72,** 4211 (1968).
31. Kogelbauer, A., master thesis, Technische Universität Wien (1987).
32. Jentys, A., Mirth, G., Schwank, J., and Lercher, J. A., "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), p. 847. Amsterdam, 1989.
33. Sanderson, R. T., "Chemical Bonds and Bond Energy." Academic Press, New York, 1976.
34. Haag, W. O., and Dessau, R. M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2., p. 305. Dechema, Frankfurt-am-Main, 1984.
35. Dyer, A., and Singh, A. P., *Zeolites* **8**(3), 242 (1988).
36. Kranilla, H., Haag, W. O., and Gates, B. C., Plenary Lecture at 11th North American Meeting of the Catalysis Society, May 1989, Dearborn, MI.
37. Mirodatos, C., and Barthomeuf, D., *J. Chem. Soc. Chem. Commun.*, 39, 1981.
38. Lago, R. M., Haag, W. O., Mikovsky, R. J., Olson, D. H., Hellring, S. D., Schmidt, K. D., and Kerr, G. T., *in* "Proceedings, 7th Int. Zeol. Conf., Tokyo 1986," p. 677. Elsevier, Amsterdam, 1986.
39. Brunner, E., Ernst, H., Freude, D., Fröhlich, T., Hunger, T., and Pfeifer, H., *Stud. Surf. Sci. Catal.* **49,** 623 (1989).
40. Fritz, P. O., and Lunsford, J. H., *J. Catal.* **118,** 85 (1989).
41. Mirodatos, C., and Barthomuef, D., *J. Catal.* **57,** 136 (1979).
42. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **107,** 451 (1987).
43. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **113,** 353 (1988).
44. Venuto, P. B., and Habib, E. T., *Catal. Rev. Sci. Eng.* **18,** 1 (1978).
45. Corma, A., Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **27,** 29 (1985).
46. Rabo, J. A., and Poutsma, M. L., *Adv. Chem. Ser.* **102,** 284 (1971).