JOURNAL OF CATALYSIS 12, 325–334 (1968)

Cracking Activity of Some Synthetic Zeolites and the Nature of the Active Sites

P. DONALD HOPKINS

From the Research and Development Department, American Oil Company, Whiting, Indiana 46394

Received July 8, 1968; revised August 30, 1968

The activities of synthetic Y faujasites, mordenites, and L zeolite for cracking *n*-hexane, *n*-heptane, and ethylbenzene were determined using a pulse microreactor. Activities of ammonium-exchanged forms after various activation procedures indicated that strong Brönsted sites were required for cracking of alkanes, but that some weaker sites may have been active for ethylbenzene cracking. Brönsted sites were also responsible for the activity of lanthanum and calcium-exchanged Y. Partial dehydroxylation increased the activity of NH_4Y for *n*-hexane cracking, but it was not possible to determine whether Lewis sites were necessary for cracking activity on any of the zeolites tested. Optimum activation temperatures for cracking of hexane by LaY and NH_4Y were similar to those found previously for benzene alkylation, suggesting common active sites for the two reactions.

INTRODUCTION

Cracking catalysts containing the zeolite class of crystalline aluminosilicates have recently become available for effecting hydrocarbon conversions. The activity of these catalysts is superior to the older amorphous silica-alumina catalysts (*1–3*); initial activities of some pure zeolites exceed those of silica-aluminas by about four orders of magnitude (*3*).

Zeolites of primary interest in catalysis contain pores large enough to admit a variety of hydrocarbon molecules. Particularly good catalysts are the synthetic zeolites, Linde X and Y, with the same structure as the mineral faujasite, and Norton Zeolon (Z) with the structure of the mineral mordenite. These are frequently supplied in the catalytically inactive sodium form. Active catalysts are forms in which the sodium has been replaced by ion exchange with polvalent cations or hydrogen. Hydrogen Zeolon (HZ) can be formed directly from NaZ by exchange with acid; NaY is unstable in acidic media but can be converted to the hydrogen form by heating the ammonium-exchange intermediate, NH_4Y (*1*). A major problem has been the determination of the nature of the catalytically active sites on zeolites. Brönsted sites (*4–7*), electrostatic fields created by polyvalent cations (*2*), Lewis sites in decationized zeolites (*8*), and Brönsted sites modified by nearby cations (*9*) have all been proposed as catalytically active sites. Both Lewis and Brönsted sites have been found in polyvalent cation forms of Y (*10, 11*) and in NH_4Y activated at elevated temperatures (*4*).

Several mechanisms have been proposed to account for Brönsted acidity in cation forms of Y. Excesses of cations (over that required by the aluminum content) which have been found in some samples of polyvalent cation exchanged forms of Y have been attributed to the incorporation of hydrolyzed species such as $CaOH^+$ (*2, 12*) which could contribute Brönsted acidity by the following mechanism:

$$CaOH^+ + Ca^{2+} + O\text{–Zeolite} \rightleftharpoons (Ca\text{–}O\text{–}Ca)^{2+} + HO\text{–Zeolite} \quad (1)$$

The existence of M–O–M groupings in synthetic faujasites has been reported (*12, 13*). For zeolites with no cation excess the following equilibrium has been postulated (*6*):

$$La(OH_2)^{3+} + O\text{–Zeolite} \rightleftharpoons La(OH)^{2+} + HO\text{–Zeolite} \quad (2)$$

Protons may also be incorporated as a result of hydrolysis of the exchange solution. Lewis acidity could arise by the same mechanism as for NH_4Y (see below) or the polyvalent cations might themselves be Lewis sites.

Creation of both types of acid sites by heating of ammonium zeolites is reasonably well understood (*1*, *14*). Brönsted sites are formed on initial heating as ammonia is driven off (deammination), leaving behind a proton localized on the zeolite skeleton as an hydroxyl group. Further heating causes dehydroxylation (or decationization) which creates positively charged (Si, Al) Lewis acid sites and negatively charged oxygens from which hydroxyl ions and protons, respectively, were removed. The charge separations represented by this picture are not stable. Charge separation is partially reduced by distribution of the negative charge on all skeletal oxygens (*15*), but further structural rearrangements may also be involved.

Data concerning deammination and dehydroxylation of zeolites have been obtained by several workers. Peri (*16*) has shown by infrared analysis that ~98% of the ammonia is removed from NH_4Y by evacuation for 1 hour at 300°C, and that NH_4Z is extensively deamminated after 1 hr at 350°C. Uytterhoeven *et al.* have shown that the hydroxyl content of NH_4Y is a maximum when evacuated at 290°C (for an undisclosed length of time) and that NH_4Y is 46% decationized at 490°C and 86% decationized at 590°C after evacuation overnight (*14*). Ward (*4*) has shown that Brönsted acidity in NH_4Y is essentially constant in the 300–500°C region after evacuation for 2 hr but that Lewis acidity increases starting at about 400°C. The low-temperature limit for dehydroxylation of NH_4Y has been reported to be about 350°C (*17*). Differential thermal analysis (DTA) has also been used to study ammonia removal from NH_4Y (*18*). Two exotherms with peaks at ~400° and 550°C were found to correspond to ammonia removal. The first exotherm started at ~300°C and was completed below 500°C at a program rate of 10°C/min. Exothermicity increased when oxygen replaced nitrogen as the blanketing gas; this was believed to be caused by ammonia oxidation.

Useful information concerning the nature of the catalytic process can be obtained from the initial activity of the catalyst, that is, the activity of the clean catalyst surface. A method particularly suitable for this involves use of the pulse microreactor as originally described by Emmett (*19*). In this method a small pulse of hydrocarbon (typically less than 0.1 ml) is passed over a small amount of fresh catalyst (less than ~1 g) and the effluent analyzed for product composition using a gas chromatograph or other instrument connected directly to the reactor. This method keeps contact times to a minimum and the results approximate the initial activity of the catalyst.

Benesi (*5*) has used this type of microreactor to study cracking of hydrocarbons by NH_4Y and NH_4Z pretreated at a series of temperatures. He observed that maximum activity was obtained with activation temperatures just above those at which the last ammonia was evolved as detected during thermogravimetric measurements under the same conditions (temperature was raised in 100°C increments), and therefore concluded that the active sites were Brönsted acids. For toluene disproportionation, maximum activity was achieved with activation temperatures, T_a, of ~600°C for NH_4Y and ~700°C for NH_4Z. For cracking of *n*-butane and *n*-pentane by NH_4Z the optimum T_a was 700°C. As T_a was increased above the optimum, activity for alkaline cracking fell off more rapidly than for toluene disproportionation.

We have performed a series of microreactor experiments similar to those of Benesi (*5*). In addition to NH_4Y and NH_4Z, we have looked at HZ and the cationic faujasites, NaY, CaY, and LaY. The hydrocarbons used, *n*-hexane, *n*-heptane, and ethylbenzene were chosen primarily to give convenient conversion levels under our test procedure. Some variation of time of activation as well as of T_a was included in our experiments. Our results support the earlier conclusions in part but suggest that only the strongest Brönsted sites are effective catalytically and that the presence of Lewis sites is either necessary or has a synergistic effect on the activity.

EXPERIMENTAL

Apparatus. The microreactor followed closely the design of Emmett (*19*). The reaction tube was a piece of ¼-inch stainless steel tube about 1 ft long. Sufficient catalyst (20–60 mesh) to make a 1-inch column, about 250 mg, was supported by a Pyrex wool plug midway through the reactor. The reactor was heated by means of a tube furnace made of stainless steel pipe wrapped with asbestos paper and nichrome wire. A control thermocouple was placed between the furnace and reactor tube and glass wool plugs were placed at each end of the furnace. A thermocouple was situated inside the reactor with its tip at the top of the catalyst bed. Hydrocarbons were introduced to the catalyst through an injection septum just upstream from the reactor. Effluent from the reactor passed directly through a short heated transfer line into a gas chromatograph.

The gas chromatograph used in the initial experiments was an Aerograph model A-90-P. This was later replaced with an F and M model 5750 to take advantage of temperature programming.

Differential thermal analysis thermograms (ΔT vs. T) were obtained on a Model DTA-DS-2 (R. L. Stone Co., Austin, Texas), in an atmosphere of nitrogen or oxygen, flowing at ~8 ml/min. Differential thermocouples were embedded in the sample and reference material (α-alumina). Temperature was programmed at 11°C/min.

Materials. The various forms of Y zeolite were prepared from a sample of NaY with a Si/Al ratio of 2.43. Cation exchange was effected by stirring three times for 6 hr with 10% solutions of metal nitrates. Excess salt was removed by stirring three times with distilled water for 6 hr. In both steps the ratio of weight of water to zeolite was about 5. Sodium analysis indicated the following percent cation exchange: NH_4Y, 74%; CaY, 72%; and LaY, 64%. Analysis of NaY revealed a 1.035 ratio of sodium to aluminum. Calcium analysis indicated the possibility of an 8% excess of calcium. Lanthanum analysis of LaY agreed with the sodium analysis. X-Ray analysis showed that no significant loss of structure occurred during cation exchange.

A sample of synthetic mordenite, designated hydrogen zeolon ultrapure powder, was used as supplied by the Norton Company; it had been spray-dried but not calcined, and had a sodium content of 0.13%. A sample of NH_4Z was prepared from NaZ using a method similar to that described for NH_4Y and had a sodium content of 0.03%. L Zeolite was supplied as KL by Linde and converted to NH_4L (66% exchange) by the same procedure as above. An amorphous silica-alumina catalyst, Nalco HA-1, was used for activity comparison.

Purities of the Phillips research grade hydrocarbons used were *n*-hexane, 99.99; *n*-heptane, 99.92; and ethylbenzene, 99.57 mole %.

Catalytic studies. The catalyst after being placed in the reactor was heated in flowing He (60 ml/min) at the activation temperature for a predetermined length of time (1 hr unless stated otherwise) and then cooled within a few minutes to the reaction temperature (350°C unless stated otherwise). After the catalyst had reached thermal equilibrium, 50 μl of hydrocarbon was introduced to the He upstream from the catalyst, and the products detected as they emerged from the reactor. Contact time with the catalyst as calculated from the geometry was about 0.4 sec. Peak width analysis indicated that only a small percentage of the alkanes remained on the catalyst more than a few seconds. No unusual product distributions were detected and carbon number distributions in the products did not change significantly with T_a. Since the carbonium ion theory predicts that propane and propylene should be the most favored initial products of hexane cracking and hydrocarbons containing three and four carbons should be the most favored initial products of heptane cracking, the size of the C_3 product fraction was taken as a measure of cracking activity. Obviously because of isomerization, secondary reactions, and alternate cracking routes, conversions were somewhat higher than calculated on the C_3 fraction. In the figures showing alkane cracking activity was measured by the ratio of total C_3 in the effluent to moles of feed injected.

Ethylbenzene was adsorbed strongly on NH_4Y so it was necessary to trap all effluent from the reactor in a U-tube section of the transfer line immersed in liquid nitrogen; after all effluent had been collected the U-tube was warmed rapidly to transfer the hydrocarbons to the gas chromatograph. Apparently ethylbenzene reacted both by dealkylation and by disproportionation. A peak, smaller than the benzene peak, appeared on the high-temperature tail of the ethylbenzene peak. Ethylene was not detected; apparently it was eluted from the reactor slowly or not at all.

RESULTS

Activity of NH_4Y. Hexane and heptane were cracked over a series of samples of NH_4Y which had been activated at various temperatures. The results are shown in Figs. 1 and 2. For both alkanes NH_4Y reached a maximum activity with T_a ~550°C and was essentially inactive with $T_a = 300°$ and 650°C; the small activity found with $T_a = 300°C$ probably resulted from additional activation when the sample was raised to the reaction temperature. With 16-hr activations at $T_a = 350°$, 425°, and 500°C activities were essentially equal and greater (~13 mole C_3/100 mole heptane) than the maximum activity (~10 mole C_3/100 mole heptane) found for 1-hr activations.

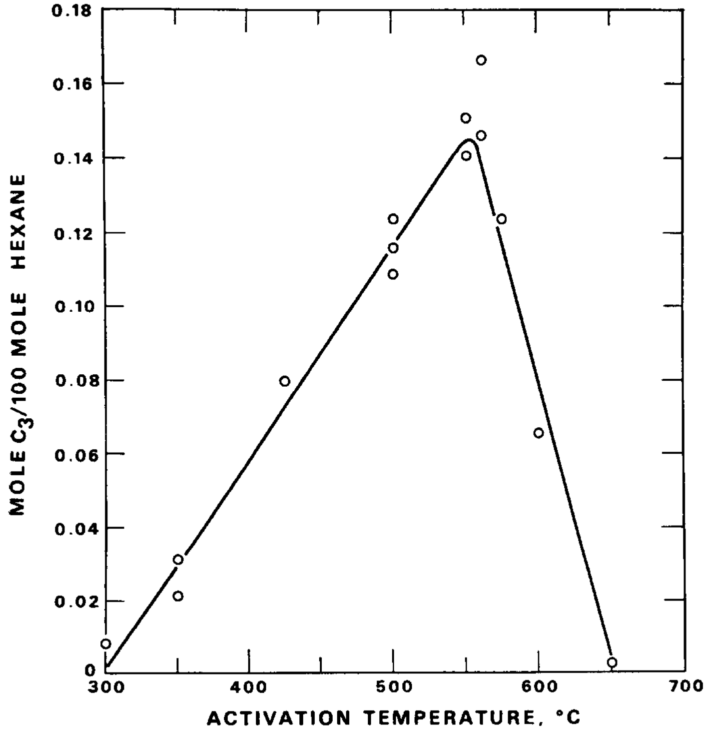

FIG. 1. Activity of NH_4Y faujasite for n-hexane cracking at 350°C as a function of activation temperature (1-hr activations).

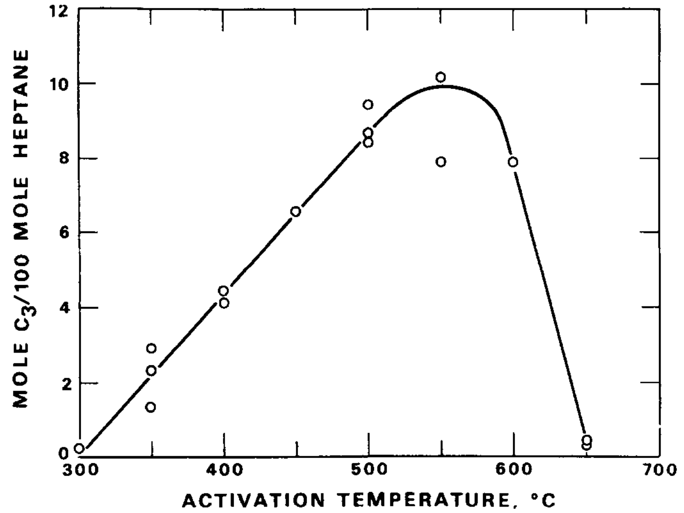

FIG. 2. Activity of NH_4Y faujasite for n-heptane cracking at 350°C as a function of activation temperatuer (1-hr activations).

Activity of NH_4Y for cracking of ethylbenzene (at 280°C) as a function of T_a was also determined.

T_a	Relative amounts in reactor effluent	
	Benzene	Ethylbenzene
300°	3	96
500°	10	91
650°	5.5	94

Although limited, these data indicate a maximum in activity at about the same T_a as for alkanes but the relative activity at $T_a = 300°$ and 650°C compared to $T_a = 500°C$ was much higher than for alkanes.

Activity of NH_4L. Cracking of heptane by NH_4L with $T_a = 350°$, 500°, and 650°C showed that NH_4L followed essentially the same activity pattern as NH_4Y. At $T_a = 500°C$ both zeolites had equal ac-

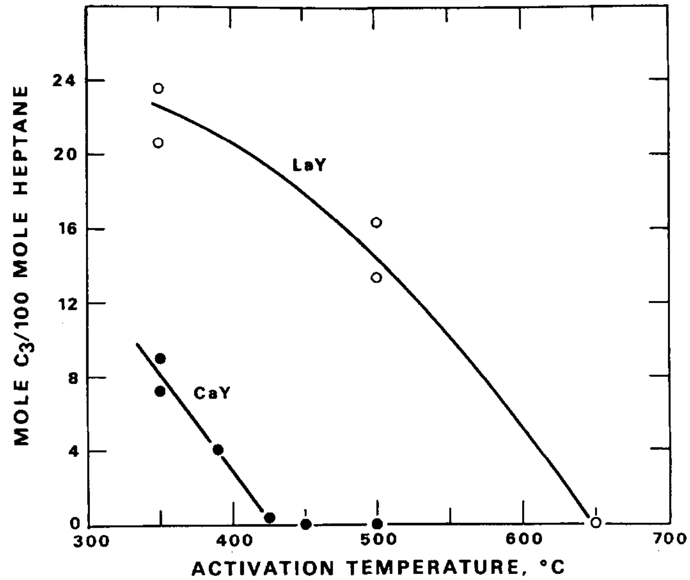

FIG. 3. Activity of CaY and LaY for n-heptane cracking at 350°C as a function of activation temperature (1-hr activations).

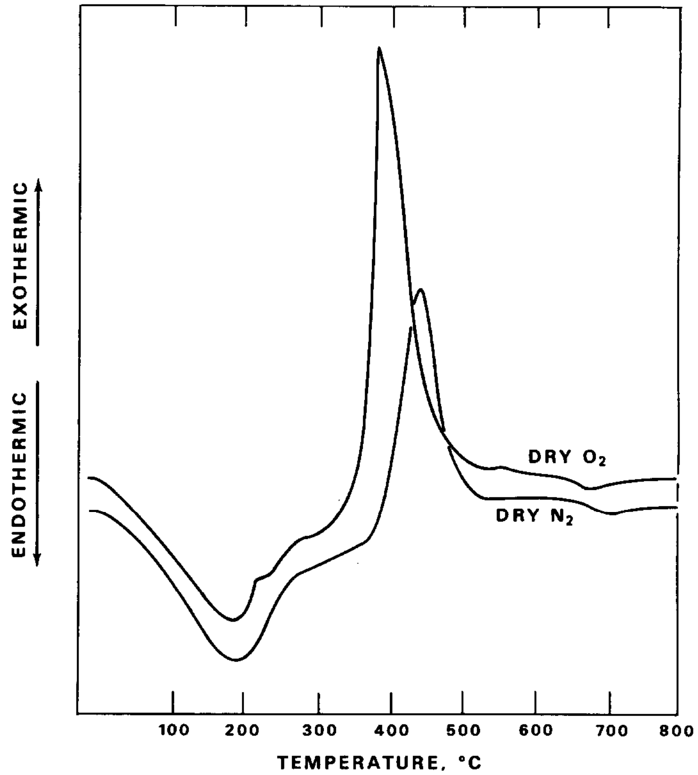

FIG. 4. Thermograms of NH_4Y in oxygen and nitrogen.

tivity, and both were essentially inactive when activated at 650°C. NH_4L was less active than NH_4Y when activated at 350°C.

Activity of cation forms of Y. CaY and LaY, unlike NH_4Y, showed no maximum in activity but a steady decrease with increasing T_a, as shown in Fig. 3. The most active form of CaY (activated at 350°C) was about as active as the most active form of NH_4Y, but LaY was about twice as active. For LaY activated at 650°C and for CaY above 425°C, no products were detected.

Under the conditions of our experiments NaY and HA-1 were essentially completely inactive. HA-1 at all activation temperatures gave heptane conversions no greater than 10^{-4} mole C_3/mole heptane.

Activity of hydrogen mordenite. The availability of both HZ and NH_4Z presented an opportunity to determine the effect of ammonia removal on activity. Representative data are shown in the following table:

Catalyst	Cracking temperature (°C)	% conversion with T_a(°C) =		
		350°	500°	650°
NH_4Z	350°	31	49	
HZ	350°	96	96	>90
HZ	300°	76	78	

The activity of HZ was essentially independent of activation temperature, but the activity of NH_4Z increased significantly when the activation temperature was increased from 350° to 500°C. The relative activity of the two catalysts should not be compared since they were prepared from different starting materials and therefore differences in sodium contents, particle sizes, and surface areas could affect activities.

DTA. Thermograms obtained for NH_4Y (Fig. 4) differed from those reported by other investigators (*4*, *18*) in that only one major exotherm instead of two appeared in the 300–700°C region. A second, very small exotherm did appear at ~550°C.

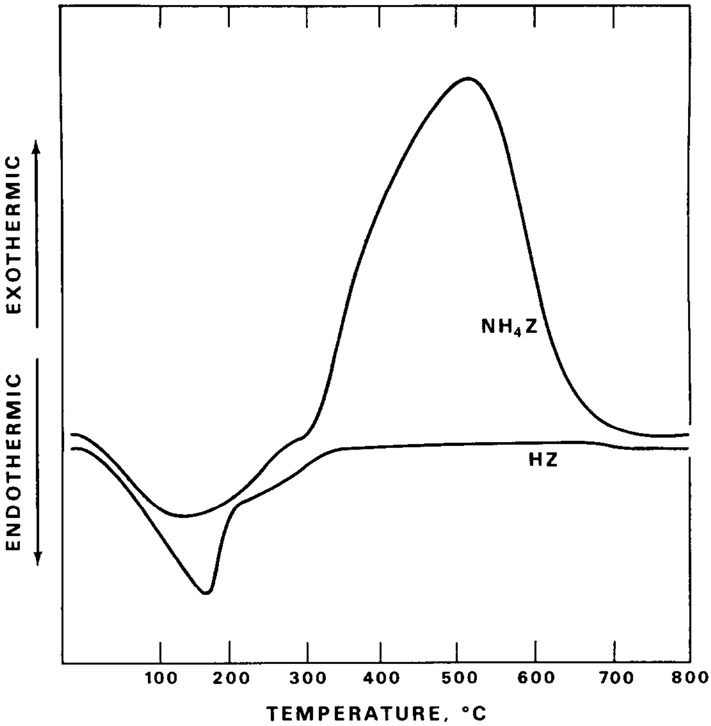

FIG. 5. Thermograms of HZ and NH_4Z in a dry nitrogen atmosphere.

The appearance of two exotherms has been attributed to removal of ammonia from two environments (*18*), one of which must be poorly populated in our sample.

During one DTA run we observed ammonia evolution beginning at 190°C and becoming more rapid near 300°C, supporting the previous conclusion (*18*) that the exotherm starting at about 300°C is associated with ammonia removal. The fact that the exotherm lies almost wholly below 500°C demonstrates that after a few minutes at this temperature in a flowing inert gas ammonia removal from our sample of NH_4Y is complete.

The sodium in our sample of NH_4Y was only 74% exchanged by ammonium but samples used by the previous workers were more completely exchanged. Thus in our sample, in contrast to the others, there was very little exchange of the 16 sodiums per unit cell (29% of the total in our sample) which are harder to exchange than the remainder and which, at least in the hydrated zeolite, occupy positions in the less accessible hexagonal prisms of the faujasite framework (*20*). Presumably the higher temperature exotherm, very small for our sample, represents removal of ammonia from the hexagonal prisms.

Changing the atmosphere from nitrogen to oxygen increased the exothermicity of the ammonia evolution peak, in agreement with Venuto *et al.* (*18*). Oxygen dried over P_2O_5 decreased the temperature at which the exothermic maximum occurred by ~60°C compared to nitrogen as shown in Fig. 4, but oxygen directly from the tank caused only a slight decrease; this is consistent with water being a product of the oxidation reaction.

Thermograms of NH_4Z and HZ, shown in Fig. 5, confirmed that the exotherm was associated with ammonia removal, since it was absent for HZ. The ammonia exotherm was wider and extended to higher temperatures than for NH_4Y, consistent with previous observations (*5*) on ammonia evolution.

DISCUSSION

The maximum in cracking activity of NH_4Y at $T_a = 550°C$ is in essential agreement with Benesi's work (*5*); the decrease in T_a for maximum activity probably was a result of the longer activation time (1 hr vs. 30 min). Benesi also showed that at higher activation temperatures the activity of NH_4Z declined more rapidly for alkane cracking than for toluene disproportionation. Our data for NH_4Y reveal the same phenomena; ethylbenzene was cracked by NH_4Y activated at 650°C, under which conditions NH_4Y was rendered inactive for alkane cracking.

Comparison of the activities of HZ and NH_4Z verify that Brönsted acidity is necessary for cracking. HZ, which required no ammonia removal, was as active when pretreated at 350°C as it was at 500°C, but NH_4Z increased in activity when activated at the higher temperature. Since the significant difference between these two materials was the presence of ammonia, the increase in activity of NH_4Z was related to ammonia removal, and therefore to formation of Brönsted acid sites.

Brönsted acidity is also necessary for NH_4Y (and NH_4L) activity, as shown by the decrease in activity when activated at temperatures above 550°C, where presumably Lewis sites are created at the expense of Brönsted sites. However, the increase in activity as T_a was raised from 350° to 550°C can not be entirely explained on the basis of creating more Brönsted sites. Results cited in the introduction and our DTA data indicate that ammonia removal from NH_4Y is rapid above ~300°C and that a 1-hr treatment at 350°C would cause extensive deammination. Particularly interesting in this respect are the data of Ward (*4*), which showed that Brönsted acidity was the same after 2 hr at either 350° or 500°C. The constant level of Brönsted acidity appears to be partially due to comparable amounts of deammination and dehydroxylation occurring as the activation temperature was increased as shown by the rise in Lewis acidity; however, the increase in the amount of Lewis acidity and therefore of deammination was small. Thus, activity increases in a region where only small numbers of either Brönsted or Lewis sites are formed.

The data can best be interpreted to mean that the strongest Brönsted sites contribute most, or all, of the activity for alkane cracking. Since both NH_4Z and NH_4Y are extensively deamminated after 1 hr at 350°C, the strong Brönsted sites which would be the last to release ammonia are not available after activation at this temperature, hence the increase in activity when T_a is raised above 350°C. (The lower activity of NH_4L at 350° seems to indicate that deammination is slower than for NH_4Y.) These sites appear to become more active in the presence of Lewis sites, as shown by the increase in activity as activation time at 500°C is increased to 16 hr. A large amount of Lewis acidity apparently is not required since the activity of NH_4Y activated 16 hr is as great at 350°C, where dehydroxylation is probably slight, as at 500°C, where dehydroxylation is ~50%. However, if only the strongest Brönsted sites were active, only a small number of Lewis sites should be required for interaction. Possibly the protonic acids became stronger through delocalization, or through the inductive effect of a nearby Lewis site. That both Brönsted and Lewis sites participate in the reaction is also possible. The possibility that Lewis acid sites are not only synergistic but necessary for catalytic activity cannot be discounted, although the activity of NH_4Y activated 1 hr at 350°C, under which conditions dehydroxylation is extremely slight, argues against their necessity.

Apparently weaker Brönsted sites (which lose ammonia more readily) are more active for dealkylation of ethylbenzene; NH_4Y activated at 350°C is relatively more active for this reaction than for cracking of alkanes, as shown by the smaller percentage increase in activity when activated at 500°C. The generally accepted mechanism for catalytic dealkylation of aromatics (*21*) involves protonation of the aromatic ring followed by loss of an alkyl carbonium ion. This reaction occurs at lower temperatures than does alkane cracking and seems more likely to involve weaker protonic acids than any postulated reaction for alkane cracking (*22*). Hence it is not surprising to find weaker sites more effective for cracking of alkylaromatics than for alkanes.

Reduction in activity of CaY and LaY with increasing activation temperature is consistent with Brönsted acidity being required for activity. Since no ammonia removal is required, Brönsted acidity should be a maximum after the lower activation temperatures. Deactivation at higher T_a probably results from shifting the equilibria of reactions (1) and (2) to the left as a result of water removal. The greater activity of LaY compared to CaY can be explained by a greater tendency of LaY to hydrolyze if both cations reacted according to Eq. (2). Alternatively, since CaY had an excess of cations and LaY did not, CaY may have reacted as in Eq. (1) and LaY as in Eq. (2) with both differences in metal ion and reaction pathway contributing to the more favorable equilibrium. By a more favorable equilibrium we mean either a greater number of acid sites, or stronger acids sites caused by the influence of the hydrolyzed ion on the proton. Enhancement of activity by cations has been postulated (*9*) to arise from polarization of the lattice electrons towards the cations, thereby producing stronger Brönsted acids from lattice hydroxyl groups. Since the polarizing powers of the cations discussed here follow the activity order, our data are consistent with this interpretation. The higher T_a required to deactivate LaY (compared to CaY) is probably a result of the greater hydrolysis tendency of La. The inactivity of NaY is expected from the low tendency of Na^+ to hydrolyze.

As with NH_4Y, the possibility that Lewis acidity is also necessary for or enhances the activity of LaY and CaY cannot be ruled out. Lewis acidity of the anhydrous metal ions increasing in the order $Na < Ca < La$ is in agreement with the observed activities.

It is interesting to note the similarity in the optimum activation temperatures for NH_4Y and LaY with those found previously for alkylation of benzene by NH_4Y and rare earth Y (REY) (*23*). For alkylation NH_4Y was most active when activated at 550–600°C (3 hr, O_2), and REY was most active after activation at 250°C. Since LaY and CaY were not activated at any temperatures below 300°C, it is possible that a maximum in cracking activity might have been found at lower activation temperatures. The similarities of the entire activity–activation temperature curves of each catalyst type for both reactions suggests that common sites are involved in the two reactions.

ACKNOWLEDGMENT

The author wishes to thank J. B. Peri for many helpful discussions and for supplying his data on deammination of zeolites.

REFERENCES

1. Rabo, J. A., Pickert, P. E., Stamires, D. N., and Boyle, J. E., *Actes Cong. Intern. Catalyse, 2ᵉ, Paris, 1960*, p. 2055, (Editions Technip, Paris, 1961).

2. Pickert, P. E., Rabo, J. A., Dempsey, E., and Schomaker, V., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, p. 714. (Interscience, New York, 1965).

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

4. Ward, J. W., *J. Catalysis* **9**, 225 (1967).

5. Benesi, H. A., *J. Catalysis* **8**, 368 (1967).

6. Venuto, P. B., Hamilton, L. A., and Landis, P. S., *J. Catalysis* **5**, 484 (1966).

7. Plank, C. J., Rosinski, E. J., and Hawthorne, W. P., Preprints, Division of Petroleum Chemistry, Vol. 9 (3), p. 325. 148th Meeting of the American Chemical Society, Chicago, Illinois, Sept., 1966.

8. Turkevich, J., Nozaki, F., and Stamires, D. N., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, p. 586. (Interscience, New York, 1965).

9. Richardson, J. T., *J. Catalysis* **9**, 182 (1967).

10. Eberly, P. E., *J. Phys. Chem.* **72**, 1042 (1968).

11. Ward, J. W., *J. Catalysis* **10**, 34 (1968).

12. Smith, J. V., Bennett, J. M., and Flanigen, E. M., *Nature* **215**, 241 (1967).

13. Olson, D. H., *J. Phys. Chem.* **72**, 1400 (1968).

14. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69**, 2117 (1965).

15. Barrer, R. M., *Ber. Bunsenges. Phys. Chem.* **69**, 786 (1965).

16. Peri, J. B., American Oil Co., private communication.

17. Tsitsishvili, G. V., Bagratishvili, G. D., Barnabishvili, D. N., and Bezhashvili, K. A., *Dokl. Akad. Nauk. SSSR* **168**, 860 (1966).

18. Venuto, P. B., Wu, E. L., and Cattanach, J., *Anal. Chem.* 38, 1266 (1966).

19. Emmett, P. H., *Advan. Catalysis* **9**, 645 (1957).

20. Sherry, H. S., *J. Phys. Chem.* **70**, 1158 (1966).

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

22. Voge, H. H., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 6, p. 452, Reinhold New York, 1958.

23. Venuto, P. B., Hamilton, L. A., Landis, P. S., and Wise, J. J., *J. Catalysis* **5**, 81 (1966).