Acidity, Catalytic Activity and Thermal Stability of Various L Zeolites

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L zeolites with various potassium, proton and aluminum contents have been prepared. Except for aluminum deficient materials the thermal stability determined from X-ray studies is decreased for heat-treated exchanged zeolites. These changes cannot explain the very important decay in acidic and catalytic properties for degrees of exchange in the range 50–75%. It is suggested that a migration of protons towards inaccessible positions may occur when cavities interconnecting the cancrinite/hexagonal prism chains become free of cations. At its maximum, for 4 K^+ per unit cell content, the catalytic activity of the L zeolites is higher than that of similarly exchanged faujasites.

INTRODUCTION

Some investigations have already been made of the properties of L type zeolite with regards to its structure (1–6), surface OH groups (7–9), adsorptive properties (2,8–16) and catalytic properties (17–19). The studies have generally been carried out either on cationated forms or on highly exchanged hydrogen forms. The hydrogen zeolites were generally studied after heating at temperature not higher than 300–400°C (9,10,12), in one case up to 650°C (18). Since it is important for many catalytic applications in the field of zeolites to obtain acidic samples stable at temperatures higher than 400°C, it was interesting to study the changes in acidity and catalytic activity upon progressive exchange of protons and to look at the thermal stability of the samples. Besides, increase in the Si/Al ratio by dealumination generally improves the properties of zeolites (20,21). So it was also worthwhile to study some dealuminated L samples.

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EXPERIMENTAL PART

Materials

The starting zeolite is KL Linde having the unit cell composition $K_8Na_{0.15}(AlO_2)_{8.4}(SiO_2)_{27}$, xH_2O. Ion exchange was performed with aqueous solutions of ammonium chloride or acetate of concentrations ranging from 0.025 to 5 M. One hour stirring was allowed for the exchange. Several treatments, up to five, were carried out to obtain a high degree of exchange. Further heating eliminated NH_3 and left protons on the surface. Prior to any measurement, all the samples were standardized by heating in dry air for 15 hr at temperatures between 300 and 700°C in conditions which avoid the ultrastabilizing effect (20). In the case of treatments at high temperatures, the zeolites were first heated at 380°C for 15 hr in order to evolve NH_3. Complete exchanges were not found under the conditions employed. This accords with the known structural characteristics of the zeolite which have some cations in small cages in which they are trapped and so are not normally exchangeable (1). The potassium content

TABLE 1

CHEMICAL COMPOSITION OF ALUMINUM
DEFICIENT L ZEOLITES

Al/uc	6.6	5.6	4
K$^+$/uc	5.1, 4.6, 4.3, 4.2, 3, 2.5, 2	5.4, 4.9, 4,5, 4.2, 3.9, 3.4, 2.5	4, 3.8, 3.6, 2.7

of the 12 samples prepared is evident from Fig. 2. Ammonium chloride or acetate treatments gave samples with identical properties.

Dealumination was made using 0.1 M HCl solutions either at room temperature or at 70°C. In the first case five treatments of 1 hr give a sample with 6.6 aluminum atoms/unit cell (uc). At 70°C five or seven successive treatments during the same time give zeolites containing, respectively, 5.6 and 4 aluminum atoms/uc. Various potassium contents were obtained by enrichment of the materials with potassium chloride solutions. The chemical compositions obtained are reported in Table 1.

The zeolites were examined by X-ray powder photography using a Guinier camera and Cu K_α radiation.

Acidity Measurements

Titration with n-butylamine or tributylamine and colored indicators chosen according to the studies of Drushel and Sommers (*22*) gave the acidity in equivalents per unit cell for several acid strengths.

Catalytic Properties

The cracking of isooctane was studied by the microcatalytic method at 450°C, by passing isooctane–hydrogen mixtures over 10 mg of catalyst which had been standardized at 550°C and heated in situ at 450°C for 15 hr in flowing hydrogen (*23*). The partial pressure of isooctane was 100 Torr, and its conversion less than 5%. The reaction products were analyzed by gas chromatography. The column used was Chromosorb PAW 80/100 mesh impreg-

nated with TCP (10%). Its temperature was 60°C and the flow rate 1.8 liters/hr. The activity is expressed either by the initial rate r_0 of formation of the main product (isobutene) (mole sec^{-1} g^{-1}) or by the amount (%) of the other products of reaction obtained in steady state conditions. These products are propene, isobutane and butenes. A slight decrease of activity during the first 5 min of a run was noted and the activity was checked at that time.

Nitrogen Adsorption

After the standardization treatment the samples were evacuated at 410°C for 15 hr. N$_2$ adsorption was performed at 77 K, and the amount adsorbed was determined by the Point B method.

RESULTS

Structure

Effect of Potassium Content

X-Ray diffraction study of the change in structure of L zeolite upon cation exchange gave results which allow the following sequences to be written. The samples are referred to by the number of potassium ions per unit cell followed by the treatment temperature (°C). Samples 8(25), 4.2(25) and 1.9(25) had nearly the same crystallinity. Some changes were noted after a 550°C heating and the following order of crystallinity was obtained: 8(25) > 8(550) ≃ 5.3(550) > 4.2(550) ≃ 3.4(550) ≃ 2.7(550) ≫ 1.9(550). The last sample was partly amorphous. The unit cell a and c parameters of many zeolites were determined and are given in Table 2. The c values do not vary significantly upon exchange of the cations while the a dimension decreases for heated samples. Hence the decay in crystallinity of the structure at high degree of exchange is accompanied by a decrease in the a parameter. Since the channel system of L zeolites parallels the c axis, a decrease in the a value affects the pore aperture. The crystallinity changes

TABLE 2
Unit Cell Parameter of Various L Zeolites

Catalysts	Pretreatment temp (°C)									
	25		300		400		550		700	
	a	c	a	c	a	c	a	c	a	c
8.4–8[a]	18.38	7.49	18.35	7.49	18.35	7.50	18.35	7.49	18.37	7.50
8.4–5.3							18.35	7.50		
8.4–4.2	18.38	7.51	18.34	7.50	18.35	7.51	18.31	7.49	18.29	7.48
8.4–1.9	18.42	7.51					18.13	7.50		
6.6–5.1							18.38	7.50		
6.6–4.3	18.33	7.51					18.36	7.51		
6.6–2.75							18.31	7.50		
5.6–4.5	18.32	7.50			18.35	7.49	18.36	7.50		
4–4.2	18.34	7.50					18.36	7.52		
4–2.7							18.32	7.50		

[a] Al content followed by K content (per unit cell).

were corroborated by infrared spectroscopy results in the structural vibration range (5) which showed a simultaneous decrease in the number of structural rings D-6 of the L structure upon cation exchange.

Effect of Temperature

The unit cell dependence on heat treatment appears also in Table 2. The c values of the samples and the a parameter for the 8 K$^+$ zeolite remain nearly constant. The a values of the Al-deficient samples are slightly increased upon heating. The crystallinity and the a dimension of the non-dealuminated material with 4.2 K$^+$/uc decreases after heating at temperatures higher than 400°C. The crystallinity of the other non-dealuminated samples with 8 or 5.3 K$^+$/uc is good up to 700°C. That of Al-deficient materials is considered below. These results are in agreement with infrared spectroscopy results (5) and with the known thermal stability of cationated L zeolites (2). Further they show that partly exchanged L zeolites are not very stable at temperatures higher than 400°C.

Effect of Aluminum Content

For zeolites containing 6.6 and 5.6 aluminum atoms/uc and various cation

amounts, the crystallinity after a 550°C treatment is good, similar to that of the L zeolites with 8 K$^+$/uc. The 4 Al/uc zeolite is not so well crystallized. Changes in the c unit cell parameter (Table 2) are not significant. The aluminum deficient samples with various cation contents have a larger a value than the parent L zeolite after the 550°C heating. This may be associated with their good crystallinity.

Nitrogen Adsorption Capacity

The micropore filling with nitrogen at 77 K of L zeolites with different degrees of cation exchange is reported in Fig. 1. Two pretreatment temperatures have been studied (400 and 550°C). The values do not
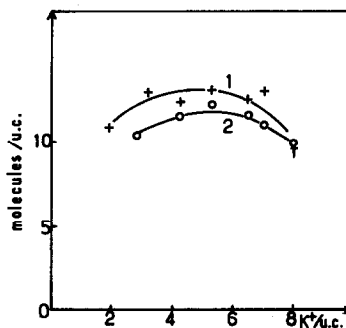

Fig. 1. Nitrogen adsorption at 77 K as a function of potassium content of non-dealuminated samples. Standard treatment at 400°C (1) and 550°C (2).

change much with the potassium content. Aluminum deficient zeolites with various cation contents give the same values as those reported in Fig. 1.

Acidity

Effect of Potassium Content

The acidity measured with n-butylamine on non-dealuminated samples heated at 550°C is reported in Fig. 2. The total acidity (limit strength $3 \times 10^{-4}\%$ H_2SO_4) is given in curve 1 of Fig. 2 and other curves report the number of acid centers with strength higher than 77% H_2SO_4 (curve 2) or 88% H_2SO_4 (curve 3).

Instead of increasing continuously as the degree of exchange proceeds, the acidity rises to a maximum near 50–60% and then decreases. Another point which arises from the curves of Fig. 2 is the parallelism of the straight parts of the lines at degrees of exchange 0–50%. Moreover, the acidity values are small compared to the number of potassium ions removed and when 4 acid sites are released, the corresponding acidity is only 0.5 equiv/uc. It is lower than the saturation capacity (2–3 molecules/uc) for molecules with a size approaching that of n-butylamine (24,25). It

was then necessary to check that n-butylamine entered the pores to titrate acid centers. Acidity experiments were carried out using tributylamine (diameter ≈ 8.1 Å) which does not penetrate the L zeolite channels (aperture 7.1–7.8 Å). Curve 4 of Fig. 2 shows that the surface acidity so measured is very small compared to n-butylamine results. Hence the linear amine can enter the pores. It was also verified that the time allowed for reactant diffusion (24 hr) is enough to reach the limit value of acidity since the result is identical after a 40 hr reaction time.

Effect of Temperature

Figure 3 reports the results of total acidity measurements after heating the non-dealuminated samples from 300 to 700°C. The smaller temperature 300°C is certainly not sufficient to decompose completely NH_4^+ ions of ammonium exchanged zeolites and some potential acid centers are not free of NH_3. Nevertheless the acidity of this sample is the highest. It may also be noted that the maximum of acidity occurs in the same range of intermediate cation content.
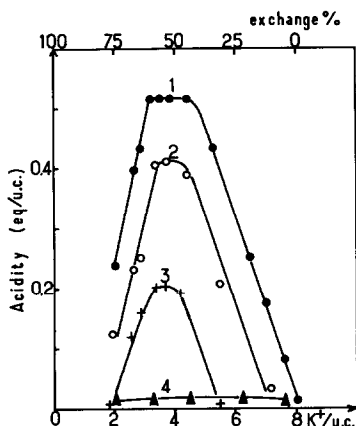
FIG. 2. Changes in acidity as a function of potassium content after 550°C pretreatments: acid strength: $3 \times 10^{-4}\%$ H_2SO_4 (1,4); 77% H_2SO_4 (2); 88% H_2SO_4 (3). Titration with n-butylamine (1,2,3) and tributylamine (4).
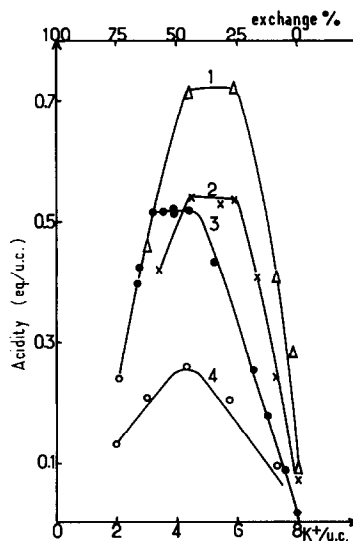
FIG. 3. Changes in total acidity as a function of potassium content after pretreatments at various temperatures (°C): (1) 300; (2) 400; (3) 550; (4) 700.
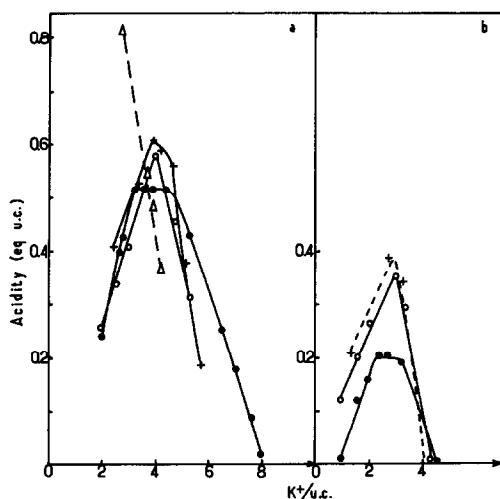
FIG. 4. Changes in acidity as a function of potassium content for various aluminum contents. (a) Total acidity; (b) strong acidity; (●) 8.4 Al/uc; (○) 6.6 Al/uc; (+) 5.6 Al/uc; (△) 4 Al/uc.

FIG. 5. Isooctane cracking as a function of potassium content (formation %): (●) isobutene; (○) isobutane; (×) propene; (△) butenes-2.

Effect of Aluminum Content

The acidity of the three aluminum deficient zeolites has been studied after 550°C pretreatments. Figure 4 reports the total acidity (Fig. 4a) and strong acidity (Fig. 4b) as a function of potassium ion content. For the samples with 8.4, 6.6 and 5.6 Al/uc the total acidity presents a maximum which is again close to 4 K^+/uc and it increases with increasing degree of dealumination. The strong acidity of these three materials (Fig. 4b) starts to develop only when the five remaining potassium ions are being exchanged.

The zeolite containing 4 Al/uc has a high acidity at low cation content (Fig. 4a). Moreover this sample shows a high residual acidity in its fully cationated form. The potassium exchange does not release strong acid sites. It has to be noted that this sample is not well crystallized.

Catalytic Activity

Effect of Cation Content

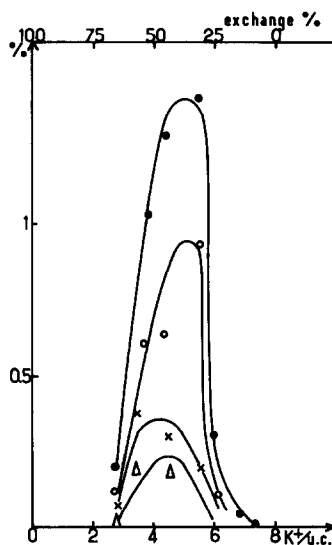The isooctane cracking results with the non-dealuminated samples pretreated at 550°C are given in Fig. 5. The formation of the several products follows parallel patterns and the catalytic activity rises to a maximum near 4 potassium ions/uc. For 2.7 cations/uc the activity is rather small. Hopkins (18) noted that a 66% exchanged L zeolite had the same heptane cracking activity as a 74% exchanged NaY type. Present results may be compared with a previous study of isooctane cracking on NaHY zeolite in the same experimental conditions (23). They are in agreement with Hopkins' work at cation exchange close to 70%. Further the maximum activity of L zeolites which occurs for a total acidity close to 0.5×10^{-3} sites/uc, i.e., 0.22 meq/g of catalyst, is about 5–10 times higher than the activity of a Y zeolite with the same number of acid sites per gram. Hence L materials are more active than Y catalysts, except of course at low cation content when L zeolite loses its properties. With both types of zeolite isobutene is the main product. It may also be noted that while KHY zeolites are several times less active than NaHY, KHL zeolites are much more active than KHY even at rather low cation contents.
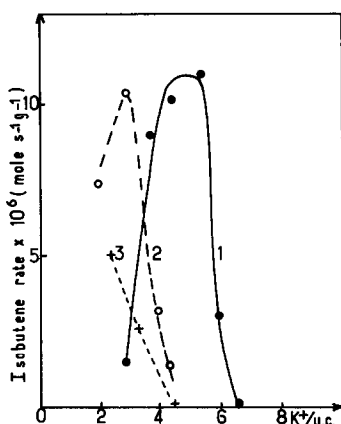
FIG. 6. Isobutene rate as a function of potassium content for various aluminum contents: (1) 8.4 Al/uc; (2) 6.6 Al/uc; (3) 5.6 Al/uc.

Effect of Aluminum Content

Figure 6 reports the changes in isobutene formation rate as a function of the cation content of the parent zeolite and of two aluminum deficient materials. The 4 Al/uc sample has no activity. The cracking properties of the 6.6 and 5.6 Al/uc zeolites reach values similar to those characterizing non-dealuminated samples, but for the same ordinate value (catalytic activity) to be achieved aluminum deficient samples have to be more exchanged. No important changes in selectivity are noted with these samples.

DISCUSSION

A general feature which characterizes most of the curves related to the acidity or catalytic activity is a maximum near 4 K^+/uc cation content. This maximum occurs after different pretreatment temperatures or for various aluminum contents. The decrease in the surface properties for cation contents, lower than 4 K^+/uc may be attributed at first to a loss in crystallinity as already shown for X type zeolites for cation exchange higher than about 50%. In the present case some highly exchanged non-dealuminated zeolites have lost a part of their crystallinity and show a decrease in unit cell parameters. But some other samples like aluminum deficient 6.6 and 5.6 zeolites are very well crystallized even in the low cation content range. Hence there is no direct correlation between the crystallinity decay and the changes in properties. Other explanations have to be invoked. Taking into account that during acidity titration or cracking the molecules of amine and isooctane enter only the main channels of the zeolite and react with sites in these channels, the modification in acidity or catalytic activity would be connected to changes occurring in the channels. Since in zeolites cracking activity is generally related to Bronsted acidity, the changes would concern protons and more probably acidic OH groups. Thermogravimetry and infrared spectroscopy have shown that the bad properties at low ion content are not related to a dehydroxylation.

As to a geometric effect, results of nitrogen adsorption show that the pore volume is kept nearly constant upon exchange, dealumination or pretreatment temperature and does not correlate with the acidity or activity properties. Some diffusion effect might also be considered for molecules going inside the particles but in fact the results described arise from two different methods. The one is a static measurement of acidity in equilibrium conditions; the other concerns the dynamic study of isooctane cracking. The diffusion effect would not lead to similar shapes of curves in the two cases. It is then more probable that the maximum in the experimental curves has to be associated with some modifications in the number of acid and active sites. Starting from a cationated zeolite, the increase in acidic and catalytic properties is explained by the release of sites. The decrease beyond the maximum implies that the sites are no more present in the channels. Two explanations may account for that. The sites may be neutralized or they become inaccessible. As to
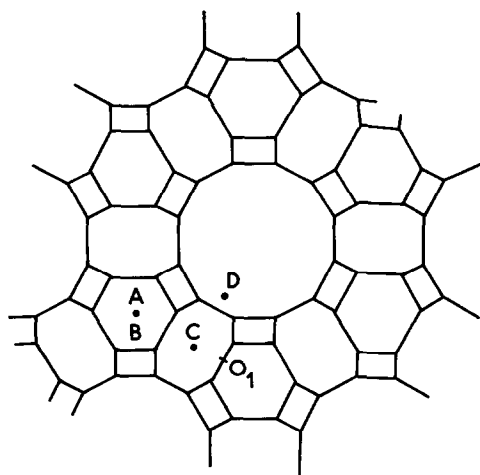
FIG. 7. Structure of L zeolite projected along c axis (1). Si or Al atoms are centered at each apex. Oxygen atoms lie about halfway between the apices (for instance oxygen atom labeled O_1). A, B, C, D are cation sites. A and B are centered in a hexagonal prism and a cancrinite cage, respectively; C is in the center of the cavity; D is in the main channel.

the first case, neutralization may arise from exchange of protons in the channels by cations coming from inner sites. At the smallest cation content (two K^+/uc) the effect would be the more important since acidity and activity are very small. Then it is not easy to understand how only two cations would be enough to neutralize nearly completely six sites. Moreover, the two remaining cations are generally supposed to be in the cancrinite cage and hexagonal prism (Fig. 7) where it is difficult to exchange them (1, this work). Then it seems improbable that these cations could easily migrate into the channels. Hence this first explanation is not quite suitable. The second hypothesis suggests that protons (active sites) may become inaccessible, i.e., become located out of the channels at low cation content. In the beginning of cation exchange, cations are removed from D sites in the channel (Fig. 7) as suggested by Barrer and Villiger (1) and protons (OH groups for instance) would be also in the channel. The acidity will increase as potassium ions are removed (right part of curves

of acidity). The next exchangeable site is C (1) which is inside a cavity connecting two chains of cancrinite cage–hexagonal prism arrangements. The protons located in this cavity, particularly if they are attached to oxygen atoms labeled 1 in Fig. 7, are inaccessible for molecules in the main channel and their acid and catalytically active character cannot be checked. The exchange of C cations would be related to the plateau of experimental curves. When the "C" cavity becomes gradually free of cations, an increasing number of oxygen O_1 may fix protons and form OH groups. It is then suggested that besides protons replacing cations in the C cavity some protons previously located in the main channel could migrate to such cavities where electrostatic environment would be better. Such proton migration would not occur if the C cavity is not free of cations. This would explain the decrease in properties (left part of curves). This preferential location of sites in inaccessible cavities would be typical of L zeolites which have framework oxygen atoms not accessible from the channel. It has to be noted that the situation is quite different from that of OH inside the sodalite cage of faujasite type zeolite. It is also worthwhile to notice that the shapes of the acidity curves do not depend on pretreatment temperature. Hence, as far as protons are related to OH groups in L zeolites, the degree of dehydroxylation is not important in determining the existence of the maximum but the cation content, i.e., the proton location, seems to be the main point. Changes in the extent of dehydroxylation could modify the ordinate and, eventually, the location of the maximum. As to this last point, the differences noted between the abscissa value of the maximum for acidity or activity curves may also be due to an influence of the reactant. In the case of the catalytic reaction, the isooctane and the products of reaction (specially olefins) might influence the static "equilibrium" location of protons

inside and outside the channels and modify the cation content which determines the proton migration in inaccessible cavities.

Besides this unexpected effect in L zeolites, some other results may be discussed. Looking at the number of acid sites released for each potassium ion exchanged in the range 0–50%, it appears from the slopes of the straight part of the curves in Fig. 2 that only 0.15 acid sites may be titrated for each cation removed. Steric hindrance may not be invoked since the 0.15 value is obtained as soon as the exchange starts when there are very few amine molecules in the channels. Moreover it is noticeable that the straight lines of Fig. 2 are parallel. Assuming no proton migration is considered at low degree of exchange, another explanation is needed. In the case of faujasite type zeolite neither accessibility nor migration could explain the similar straight parallel lines obtained for acidity as a function of exchange and for several acid strengths. It was concluded that a new effect, an efficiency of sites due to the interactions of sites with the charged atoms of the structure located in the walls of the cavities, had to be considered in zeolites. This efficiency, defined by a coefficient ranging from zero to one, reduces the titrability of the sites (26) and is increasing upon dealumination. The same effect was found again in adsorption studies. Considering the slope of 0.15 for curves of Fig. 2 and the increase of the slopes as aluminum is removed from the zeolite (Fig. 4), the efficiency of sites certainly accounts for a large part of the results with L zeolite.

The behavior of the 4 Al/uc sample suggests some further comments. When this material contains 4 potassium ions/uc it would have no more acid sites. In fact it shows a rather important residual acidity. Since the zeolite has been obtained from the sample having 2.7 K^+/uc in which potassium ions have been incorporated, it is suggested that a part of these additional

cations are located in small cavities and they should not influence the concentration of acid sites. Some comparable results were described on Y zeolites (27,28). Another interesting feature is the lack of any decrease in acidity at low cation level. In this catalyst the process of proton migration towards inner sites would be avoided.

In conclusion, the unexpected very low acidic and catalytic properties of L zeolites when highly exchanged may be explained by the particular structure of this material which contains oxygen atoms able to give OH groups which are completely inaccessible.

ACKNOWLEDGMENTS

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