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The Role of Polyvalent Cations in Developing Strong Acidity: A Study of Lanthanum-Exchanged Zeolites

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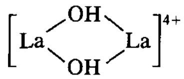
A series of faujasite and ZSM-20 zeolites was prepared such that they had a minimum amount of extraframework aluminum, but a range of Si/Al ratios. These materials were relatively inactive for the hexane cracking reaction, which was used as a test of strong acidity. When La^{3+} ions had been exchanged into the zeolites, the cracking activity first increased with respect to lanthanum loading and then went through a maximum. When the maxima were plotted as a function of the framework aluminum content, Al_f, for the series of zeolites, the activities increased until Al_f was ca. 35 per u.c. and then decreased below a measurable level with zeolite X. The change in activity with respect to Al_f paralleled that observed with steam-dealuminated zeolites, but the absolute activities of the La-exchanged samples were less. These results are consistent with a model of strong acidity in which both the Al_f distribution and the presence of polyvalent cations in the β cages are important. Lanthanum ions in the form of  $\left[\mathrm{La}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\mathrm{La}\right]^{4+}$ or $La(OH)^{2+}$ species are believed to be responsible for the withdrawal of electrons from the framework hydroxyl groups, thus making the protons more acidic. © 1990 Academic Press, Inc.

INTRODUCTION

It is now recognized that a normal H-Y zeolite, with its full complement of protons, is a relatively inactive catalyst for such hydrocarbon reactions as cumene dealkylation and hexane cracking (*1*, *2*). But when this material is dehydroxylated at elevated temperatures, steamed, or treated with $SiCl_4$, a considerably more active catalyst is obtained. Each of these treatments, which generically are referred to as dealumination, not only removes aluminum from the lattice, but also deposits extraframework aluminum within the cavities of the zeolite. Thus, two factors might be important in effecting the enhanced activity of a dealuminated zeolite: (i) the change in the distribution of the framework aluminum and (ii) the presence of extraframework aluminum. If one assumes that the activity of the zeolite is indicative of the acidity, then one may conclude that whereas the number of acid sites has decreased (the extensive factor), the strength of the remaining acid sites has increased considerably (the intensive factor) (*3*).

Early theoretical arguments of Dempsey (*4*) and also of Mikovsky and Marshall (*5*) suggested that the acid strength was related to the Al distribution in the framework and that only Al atoms with no second-neighbor Al atoms in the 4-rings are responsible for strong Brønsted acidity. Using statistical models Beagley *et al.* (*6*) derived a distribution for isolated Al atoms, $N(0)$, as a function of the total number of framework Al atoms per unit cell, Al_f. If one chooses a model which emphasizes the repulsion between Al_f atoms, $N(0)$ increases linearly with respect to Al_f, up to 32 Al_f/u.c. and then decreases to zero at 64 Al_f/u.c. Several studies have now confirmed the linear increase in activity up to ca. 32 Al_f/u.c., (*1*, *2*, *7*), but dealuminated zeolites having higher Al_f values have been difficult to obtain with

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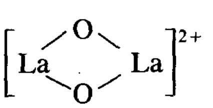
good crystallinity. A normal H-Y zeolite exhibits even less activity than would be predicted on the basis of $N(0)$ at ca. 54 Al/u.c. (*2*).

Although the experimental results support the role of the framework aluminum distribution in determining acidity, there has been considerable speculation that other factors such as extraframework aluminum may also be important. Beyerlein *et al.* (*7*) recently provided experimental evidence that such extraframework aluminum might be important. This group showed that a sample dealuminated by treatment with ammonium hexafluorosilicate (AHF) exhibited much less carbonium ion activity for isobutane conversion than might be expected, based on the number of framework Al atoms. This treatment leaves very little extraframework Al in the zeolite. When the sample was mildly steamed the activity became considerably greater. The authors concluded that the enhanced acidity was a result of a synergism between the framework Brønsted sites and Lewis sites associated with extraframework aluminum. Fritz and Lunsford (*9*), as well as Lombardo *et al.* (*10*), have suggested that the significant extraframework aluminum might exist in the β cages as cations that are bridge-bonded through oxygen atoms. With such cationic species being present in only part of the β cages and with the cations providing partial charge compensation for the Al_f tetrahedra, the concentration of strongly acidic Brønsted sites need not be equivalent to the concentration of Al_f.

The hypothesis that one strongly acidic proton is associated with each $N(0)$ Al atom also is inadequate to explain the effects of poisoning with Na^+ or NH_4^+ ions and the hydroxyl infrared spectra of dealuminated zeolite-Y. By observing the effect of Na^+ on catalytic activity Beyerlein *et al.* (*8*) and more recently Fritz and Lunsford (*9*) demonstrated that the number of strongly acidic centers was only one-third to one-fifth the number of Al_f atoms. On the basis of NH_4^+ poisoning experiments Hall and coworkers (*10*) concluded that approximately 10% of the potential Brønsted sites, counted as Al_f ions, were involved in the catalytic decomposition of neopentane. Moreover, the infrared spectra of dealuminated zeolites indicated that several hydroxyl species of different acidities were present in a dealuminated zeolite (*9*). Several types of protons were associated with framework oxygen and others were associated with extraframework aluminum oxides or oxyhydroxides.

The complexity of the usual dealuminated zeolites makes it difficult to separate the factors that may be important in effecting strong acidity. Ideally one would like to ion-exchange Al^{3+} into a series of faujasite-type zeolites that had been synthesized with Al_f from 0 to 65 per u.c., but this clearly is not possible for two reasons. First, Al^{3+} hydrolyzes extensively, and it is difficult to carry out an aqueous exchange with this simple ion. Second, faujasite-type zeolites have not been synthesized over this extended range. As an alternate approach we have studied a series of lanthanum-exchanged zeolites having a rather broad range of Al_f, but a minimum amount of extraframework aluminum. These include normal X and Y zeolites, ZSM-20, which is a close structural analog of the faujasites (*11*), and Y-type zeolites dealuminated with AHF.

Lanthanum-exchanged zeolites are particularly attractive for such a fundamental study because of the structural information which is available on the location of the cations. At room temperature a maximum of 13 La^{3+}/u.c. is incorporated into zeolite-Y, and these remain in the large cavities because of their hydration sphere. When the zeolites are heated to approximately 300°C, the hydration sphere is lost and the lanthanum ions migrate into the β cages where they are preferentially attached to sites I′ (*12*). Some of the water molecules react with the ions to form dilanthanum oxy and hydroxy species having a lower effective positive charge. Species such as



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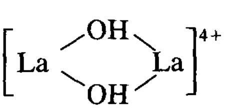


have been proposed, and these are analogous to the aluminum species that are believed to be responsible, in part, for the strong acidity in dealuminated zeolite-Y. Rees and Tao (*13*) concluded that part of the lanthanum is present in site I as La^{3+} ions. By contrast, a neutron diffraction study of a La-Y zeolite dehydrated at 600°C demonstrated that the lanthanum was located at site I′ and confirmed the presence of nonframework oxygen atoms bonded to the lanthanum (*14*). Moreover, the study showed that a single proton was attached to the oxygen.

EXPERIMENTAL

Six different zeolites were used throughout this work. H-X(78) and H-Y(54) were X- and Y-type zeolites with 78 and 54 Al/u.c., respectively, provided by Union Carbide. H-Y(50) was a Y-type zeolite with a framework aluminum content of 50 atoms per unit cell, provided by Akzo Chemie. H-Y(21) and H-Y(35) were zeolites obtained from Y(54) by dealumination with the chelating agent ammonium hexafluorosilicate. They had an aluminum content of 21 and 35 Al/u.c., respectively. ZSM-20, which had an aluminum content of 42 Al/u.c., was prepared using a modification of the method reported by Derouane *et al.* (*15*). Several dealuminated Y-type zeolites, prepared either by steaming or by treatment with silicon tetrachloride, were used for comparison.

Zeolites dealuminated with AHF were prepared using a variation of the method of Skeels and Breck (*16*). A 10-g sample of the zeolite was slurried in 100 ml of deionized water and heated between 75 and 95°C. To this slurry a 1 *M* solution of AHF was added at a rate of 0.005 mol reactant per mole aluminum per minute with stirring. The total amount of solution added depended on the desired degree of dealumination; the calculated amount of aluminum, based on stoichiometry, generally was extracted. The resultant slurry was maintained at 75 to 95°C for 2–3 h with stirring, then filtered while hot and washed with 1 liter of hot water to eliminate fluorides.

Prior to lanthanum exchange into the zeolites, sodium was completely removed with excess ammonium cations by slurrying 10 g of the zeolite in 1 liter of 1 *M* ammonium nitrate solution at 70°C for 24 h with stirring. The slurry was then filtered and washed with 1 liter of deionized water. This procedure was repeated five times. The final product was dried at 120°C for 24 h in air. A calculated amount of $La(NO_3)_3$ was dissolved in 1 liter of deionized water, and the ammonium ion-exchanged zeolites were then mixed with this solution and kept at 70°C, with stirring, for 24 h. Approximately 80% of the La^{3+} in solution was exchanged into the zeolite. The product was then filtered, washed with 1 liter of deionized water, and dried in air at 120°C for 24 h.

Total analysis of the zeolites was carried out by dissolving the samples in a solution of hydrofluoric acid and perchloric acid. The solutions were heated on a hot plate until they were dry, and the residue was dissolved in water. The resulting solution was analyzed for Na^+, Al^{3+}, and La^{3+} by the ion-coupled plasma method, using an ARL 3510 ICP spectrometer. The framework aluminum content was determined from the ^{29}Si solid-state NMR spectrum. Spectra were acquired using a Bruker MSL-300 spectrometer.

As indicated in Table 1 the crystallinity of all samples, determined by XRD, was close to 90% before reaction, with only the HLa-Y(21) sample having lower crystallinity (84%). The lower crystallinity of HLa-Y(21) may result from its highly dealuminated structure. During dealumination with ammonium hexafluorosilicate, silicon insertion proceeds much more slowly than aluminum extraction, and even under optimum conditions silicon insertion may not be achieved completely. After reaction the crystallinity

TABLE 1

Degree of Crystallinity for Fresh and Used Lanthanum-Exchanged Zeolites

Zeolite	Crystallinity before use (%)	Crystallinity after use (%)
HLa-Y(54)	93	86
HLa-Y(50)	92	84
HLa-ZSM-20(42)	96	90
HLa-Y(21)	84	78
HLa-X	94	75

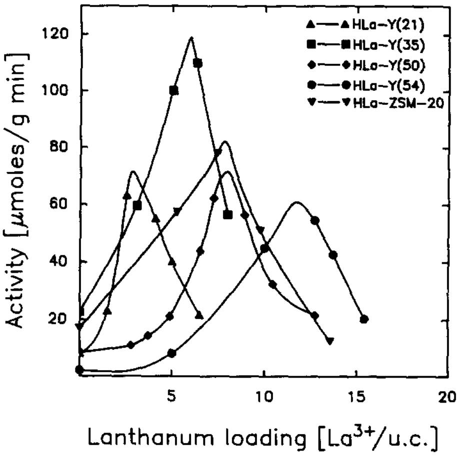


FIG. 1. Variation in hexane cracking activity at 400°C as a function of lanthanum exchange for HLa-Y(21), HLa-Y(35), HLa-ZSM-20, HLa-Y(50) and HLa-Y(54) zeolites.

of all the zeolites decreased somewhat. The HLa-X zeolite was particularly susceptible to loss in crystallinity on exposure to the water vapor in air; therefore the zeolite was converted to the ammonium form before removal from the reactor.

The presence of acid sites and La^{3+} in the large cavities was determined from the ^{31}P solid-state NMR spectrum of adsorbed trimethylphosphine (TMP) which was used as a probe molecule. Approximately 0.3 g of zeolite was dehydrated under vacuum (10^{-6} Torr) at 100, 200, and 300°C for 1 h each and at 400°C for 2 h. The sample was heated between these temperatures at a rate of 2°C/min. After dehydration, TMP was adsorbed from the gas phase at room temperature at a pressure of 50 to 75 Torr for 1 h. Excess TMP was removed by evacuation for 30 min. The samples were packed in zirconium oxide rotors, under argon in a glovebox. Proton-coupled and decoupled ^{31}P spectra were acquired with cross polarization while the sample was spun at the magic angle at a frequency of 3.0 or 3.4 kHz. Nitrogen was used as the drive gas.

The hexane cracking activity was determined using a quartz U-tube reactor with an internal diameter of 5 mm. Between 40 and 45 mg of the catalyst in the form of 20 to 45-mesh-size chips were placed in one arm of the reactor on top of quartz chips, which served to preheat the gases. The zeolite was dehydrated carefully under flowing nitrogen (20 ml/min) at 100°C for 1 h, at 200 and 300°C for 40 min each, and at 400°C for 2 h. After activation of the catalyst the reactor was bypassed, but kept at 400°C for 30 min, while the nitrogen was directed through a hexane saturator at 0°C. The hexane flow (ca. 20 ml/min total flow) was then passed through the reactor with the catalyst at 400°C. After 5 min on stream a gas sample was injected into the GC. Nitrogen was used as an internal standard. The activity, based on the weight of hydrated zeolite, was determined from the weighted sum of the products, including small amounts of C_6 isomers. A Carle AGC-111 gas chromatograph with a 3-m Porpack N column (80–100 mesh), operated isothermally at 145°C, was used for the analysis of the cracking products.

RESULTS AND DISCUSSION

Catalytic properties. The effect of lanthanum content on hexane cracking activity for five different zeolite modifications is shown in Fig. 1. For each of the zeolites the activities reached a maximum and subsequently decreased with the addition of increasing amounts of lanthanum. The maximum activity was obtained at different lanthanum concentrations for each zeolite. For Y(54) the maximum activity was obtaind at a lantha-

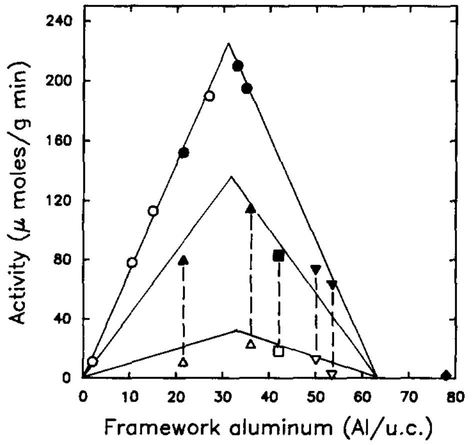


FIG. 2. Hexane cracking activity as a function of framework aluminum content: ○, Y-type zeolite dealuminated with $SiCl_4$; ●, Y-type zeolite prepared by steaming; △, Y-type zeolite dealuminated with ammonium hexafluorosilicate; ▲, after La^{3+} exchange to level of maximum activity; □, ZSM-20; ■, after La^{3+} exchange to level of maximum activity; ▽, as synthesized zeolite Y; ▼, after exchange to level of maximum activity; ◆, HLa-X.

nide concentration of approximately 12 cations per unit cell. The activity of this zeolite increased from approximately 2 μmol/g min to almost 62 μmol/g min. For all of the zeolites except X(78) the maximum activity occurred when the La^{3+} content was about 20% of the framework Al content. The X(78) zeolite, both in its hydrogen form and after lanthanum exchange, did not exhibit any measurable activity. A second series of partially lanthanum-exchanged samples prepared by an identical procedure gave similar results, indicating a reproducible effect of lanthanum on the acidity of zeolites. The zeolites without lanthanum exchange are labeled the protonic form (e.g., H-Y(54) for the Y(54) zeolite), while the zeolites partially exchanged with lanthanum to the level of maximum activity are labeled HLa-forms (e.g., HLa-Y(54) for the Y(54) zeolite).

The maxima in the activity curves of Fig. 1 are plotted in Fig. 2 as a function of the framework aluminum content. For comparison the activities of the same series of zeolites in the hydrogen form are included, as well as a series of H-Y zeolites that were prepared by dealumination with steam or $SiCl_4$. The latter series also had not been lanthanum-exchanged. The solid lines represent the functional relationship between $N(0)$, the number of isolated Al_f atoms, and Al_f. Clearly, the three sets of data are fit reasonably well by this functional relationship. In agreement with the results of Beyerlein *et al.* (*7*) we find that the zeolites having the same framework Al content, but without extraframework aluminum, are much less active than those having extraframework aluminum. But in all cases the maximum activity appears to occur at about 32 Al_f/u.c. Thus, as pointed out previously (*9*), the presence of isolated Al_f atoms is a necessary but not sufficient condition for achieving high acidity. The current results with lanthanum-exchanged zeolites indicate that polyvalent cations residing in the sodalite cages also are essential for the formation of strong acidity. These cations interact with the framework via a polarizing or inductive effect, withdrawing electrons from the O–H bonds. The result is a stronger Brønsted acid. Obviously, the lanthanum species are not as effective as the analogous aluminum species in generating strong acidity, and this is not surprising since lanthanum has a larger ionic radius, which means that the outer electron shell is more diffuse. The charge/radius ratios for La^{3+} and Al^{3+} are 2.95 and 5.88 $Å^{-1}$, respectively, therefore the polarizing effect of aluminum would be greater.

The amount of framework aluminum, as well as the number of lanthanum cations and protons, is given in Table 2. The amount of lanthanum necessary for maximum activity in the different zeolites was rather small compared to the larger amounts of framework aluminum atoms present in the zeolites. Most of the samples showed maximum activity for a La^{3+} level equal to or less than eight per unit cell.

The activity curves in Fig. 1 can be understood within the framework of a model for

TABLE 2

Framework Aluminum Content and Charge-Balancing Cations for Lanthanum-Exchanged Zeolites[a]

Zeolite	Al_f	La^{3+}	La equiv.[b]	H^+	Activity (μmol/g · min)
HLa-Y(54)	54	11.61	29	25	60.96
HLa-Y(50)	50	8.26	21	29	72.02
HLa-ZSM-20	42	8.04	20	22	81.18
HLa-Y(35)	35	5.92	15	20	117.16
HLa-Y(21)	21	3.11	8	13	70.25

[a] All concentrations per unit cell.
[b] Assuming an equivalent charge of +2.5.

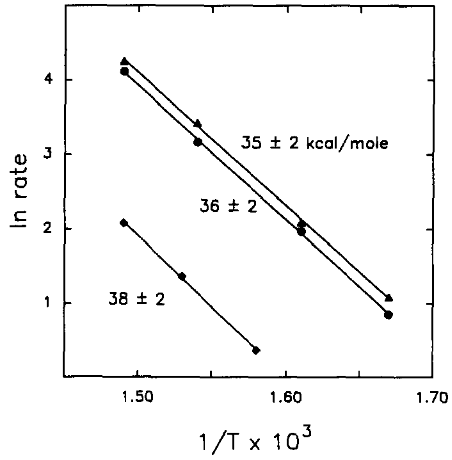


FIG. 3. Arrhenius plots for (◆) H-Y(21), (▲) HLa-Y(21), and (●) HLa-Y(54) zeolites.

strong acidity in zeolites that involves both the requirement of isolated Al_f atoms and the presence of polyvalent cations in the β cages. Considering first the zeolite H-Y(35), as lanthanum enters the sodalite cages the protons associated with that cage would become strongly acidic, but at the same time there are fewer protons after ion exchange. For example, at a loading of 10 La^{3+}/u.c. there would be only 10 H^+/u.c. remaining, assuming an equivalent charge of 2.5 (*12*), and of those 10 H^+/u.c. some would not be in cavities containing lanthanum. In the H-Y(54) zeolite not all of the protons are associated with isolated Al_f, therefore part of the lanthanum is ineffective in generating strong acidity. This phenomenon was manifested in the small effect that the first 5 La^{3+}/u.c. had on activity. The absence of catalytic activity in the HLa-X zeolite is an example of the need for *both* the polyvalent cation and isolated Al_f.

Aldridge *et al.* (*17*) observed that in a static system at 338°C the rate of conversion of hexane over a fully exchanged La-X zeolite was about two-orders of magnitude less than the maximum activity reported here for a lanthanum-exchanged zeolite. Moreover, it was observed in the earlier study that the activity decreased significantly when the zeolite was heated above 340°C. These results, in general, agree with the immeasurably low activity of the HLa-X zeolite that we have found in our flow apparatus.

The activity of the zeolites containing neither lanthanum nor any apparent extra-framework aluminum was surprising. It is likely that a small amount of dealumination occurred during the activation of the catalysts at 400°C, and this was responsible for the limited hexane cracking activity.

The activation energy for the reaction was determined for three different catalysts from the data of Fig. 3 and was found to be 35 ± 2 kcal/mol for HLa-Y(21), 36 ± 2 kcal/mol for HLa-Y(54) and 38 ± 2 kcal/mol for H-Y(21). These values may be compared with activation energies of 34–36 ± 4 kcal/mol which were observed in this laboratory for hexane cracking over dealuminated zeolites (*9*). The comparable activation energies suggest that acid centers of similar strengths are present in dealuminated and HLa-Y zeolites, which is in conflict with the proposed model. The error in determination of the activation energies, however, may obscure differences in acid strength.

n-Hexane is a good model compound, as strong acid sites are necessary to crack it, and the products formed are composed of C_6 and lighter materials, allowing an easy product separation and analysis. The dilution of *n*-hexane with the nitrogen carrier avoided heavy coking of the zeolite and resulted in a low conversion necessary to pre-

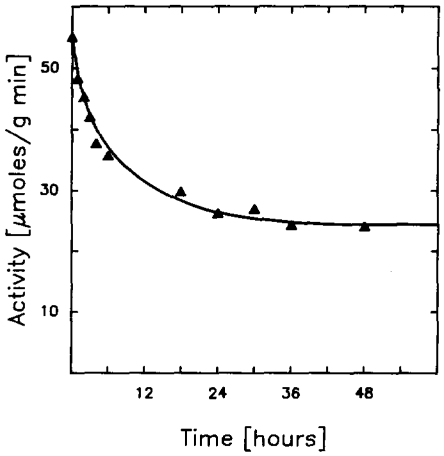


FIG. 4. Deactivation of HLa-ZSM-20 as a function of time on stream.

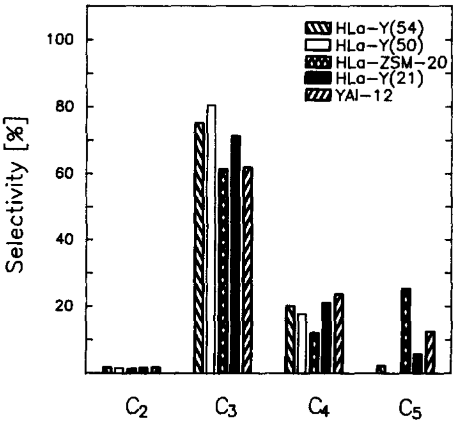


FIG. 5. Product distributions from *n*-hexane cracking over different zeolites at a conversion level of ca. 6%.

vent mass and heat transport effects. The product distribution and amount of products from the cracking over the zeolite were measured after 5 min of reaction time, during which the decrease in activity was minimal. As shown in Fig. 4 the activity decreased for up to 12 h, before reaching steady state at approximately 45% of the initial activity.

Variations in product distributions were observed for the different zeolites, for a conversion of ca. 6%. The catalysts, HLa-Y(54), HLa-Y(50), HLa-ZSM-20, HLa-Y(21), and a zeolite dealuminated with $SiCl_4$ with an aluminum content of approximately 12 framework atoms per unit cell (YAl-12), had a similar C_2 production, while the amounts of C_3, C_4, and C_5 varied as shown in Fig. 5. No products with molecular weights larger than the original C_6 were observed, although small amounts of C_6 isomers were found. The highest C_3 production was observed with the HLa-Y(50) zeolite, although it was close to those observed for HLa-Y(54) and HLa-Y(21).HLa-ZSM-20 and YAl-12 had a slightly lower C_3 production, but the C_3 fraction was still the major product of the reaction. The C_4 production was similar for the different catalysts, and only HLa-ZSM-20 showed a lower C_4 formation. The amounts of C_5 obtained for the different catalysts showed the largest variations, with the highest rate of formation being obtained with the HLa-ZSM-20 catalyst. No C_5 compounds were detected for the HLa-Y(50) zeolite.

Catalyst characterization. The infrared spectra in the hydroxyl region did not reveal any features that might be correlated with catalytic activity. In particular, a band at ca. 3600 cm^{-1} which previously was attributed to a strongly acidic proton, first in a La-X zeolite (*17*) and more recently in dealuminated zeolites (*9*), was not consistently present in these samples. The H-Y(54) sample exhibited the usual three bands at 3550, 3640, and 3740 cm^{-1}. Following the exchange of La^{3+} into the zeolite the broad band at 3550 cm^{-1} was resolved into a peak at 3540 cm^{-1} and a shoulder at 3565 cm^{-1}. A weak shoulder also became apparent at 3615 cm^{-1}. The dealuminated zeolites, exchanged to the level of maximum activity, where characterized by the same three bands observed in the H-Y(54) sample; however, there was considerable intensity in the 3600 cm^{-1} region and the 3640 cm^{-1} band was shifted to about 3630 cm^{-1}. A weak band due to highly acidic protons could have been obscured by the rather broad bands of the less acidic hydroxyl groups.

The ^{31}P solid-state NMR spectrum of tri-

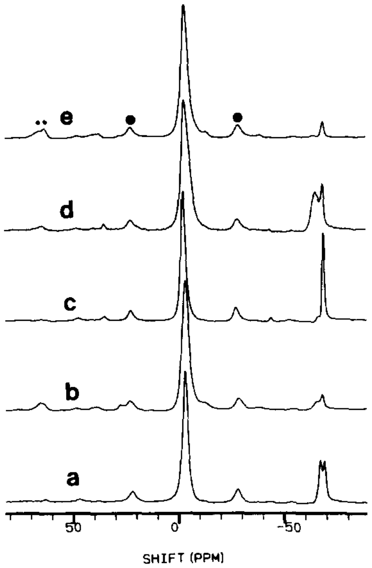
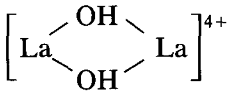


FIG. 6. Proton-decoupled ^{31}P NMR spectra of trimethylphosphine adsorbed in zeolites: (a) HLa-Y(54), (b) HLa-Y(21), (c) HLa-Y(50), (d) HLa-ZSM-20, (e) HLa-Y(35). ● denotes spinning side bands.

methylphosphine (TMP) has been effectively used to probe acid sites in zeolite-Y (*18*, *19*). Interaction of $(CH_3)_3P$ with a Brønsted site in a zeolite gives rise to the protonated adduct, $[(CH_3)_3P\text{-}H]^+$, which has a chemical shift of -2 to -4 ppm, and a $J_{P\text{-}H}$ coupling of ca. 550 Hz. Trimethylphosphine coordinated to Lewis acid sites has a resonance at -62 ppm, and even interaction with Na^+ ions may be probed by the presence of a resonance at -60 ppm. The spectrum of liquid-like TMP in the zeolite is at -67 to -68 ppm.

The proton-decoupled NMR spectra of TMP in the lanthanum-exchanged zeolites are shown in Fig. 6. In addition to the resonance of the protonated adduct at -3 ppm the resonance of liquidlike TMP at -67.8 ppm is common to all spectra. Weak resonances at 38–42 ppm are attributed to solid-like and physisorbed trimethylphosphine oxide that is formed by the inadvertent oxidation of TMP (*20*). A resonance at ca. -63 ppm varies in intensity from one sample to another. This resonance, which was greatest for the HLa-Y(54) and HLa-ZSM-20 zeolites, did not appear to be related to catalytic activity. The resonance at -63 ppm could result from TMP interacting with an aluminum Lewis acid site; however, more likely, it results from the interaction between TMP and a small amount of lanthanum present in the large cavities of the zeolite. Trimethylphosphine is much too large to enter the β cages. These NMR results confirm that lanthanum ions are found mainly in the β cages and therefore are involved in catalysis in an important but indirect manner.

CONCLUSIONS

These results support a model for strong acidity in Y-type zeolites which includes both isolated framework aluminum atoms, i.e., atoms without next-nearest tetrahedral aluminum neighbors, and the presence of polyvalent cations in the β cages. Considering the HLa-Y(35) zeolite as an example, one has a case where essentially all of the Al_f atoms are isolated, so the framework distribution is not a factor. If one examines two β cages, on the average there would be about nine Al_f atoms, two La ions, and five protons (Table 2). Five Al_f atoms would be present in one β cage and four in the other. In the β cage containing five Al_f atoms the two La ions could reside as a  $\left[\mathrm{La}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}}\mathrm{La}\right]^{4+}$ species that would serve to compensate for the charge on 4 Al_f tetrahedra, and the remaining proton would be strongly acidic. The other β cage would have four Al_f atoms and four weakly acidic protons. Thus, out of nine Al_f atoms only one would be associated with a strongly acidic proton, which is in agreement with the NH_4^+ ion poisoning experiments of Hall and co-workers (*10*). As an alternative the La ions could be present in the β cages as $La(OH)^{2+}$, in which case there would be three strongly acidic protons out of seven total protons, or nine Al_f atoms. The ratio of strongly acidic protons to Al_f atoms is in agreement with the Na^+ poisoning studies of Beyerlein *et al.* (*8*). For the model to be applicable at lower Al_f content there must be a finite probability of having β cages that contain at least three or five Al_f atoms, depending on the form of the complex La ion. The type of complex polyvalent ion may, in fact, result in subsets of strongly acidic sites which might be distinguishable by different probe molecules such as neopentane (*10*), isobutane (*7*), and *n*-hexane (*9*), and by different reaction conditions. The inductive effects of the highly charged polyvalent cation complex on the O–H bonds of the framework hydroxyl groups are inferred; thus, it would be useful to carry out theoretical calculations based on this model.

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