JOURNAL OF CATALYSIS 24, 262-271 (1972)

The Physical Properties and Catalytic Activity of AlHY Zeolites

K. M. WANG AND J. H. LUNSFORD

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received April 20, 1971

A series of AlHY zeolites has been prepared in which the original sodium ion was replaced by aluminum and hydrogen ions in varying concentrations. These zeolites show greater initial activity for the disproportionation of toluene than an acidic zeolite prepared from NH_4Y zeolite; however, the activity decreases to the level of NH_4Y upon the addition of more toluene. It is possible to introduce up to 16 exchangeable aluminum ions per unit cell, which is more than the number found in an ultrastable zeolite. In contrast to the ultrastable zeolite no aluminum is removed from the lattice during the formation of the AlHY zeolites. The AlHY zeolites are unstable to hydrothermal treatment. Infrared studies show that the number of hydroxyl groups with stretching frequencies at 3640 and 3540 cm^{-1} decreased as the aluminum exchange increased. No band at 3600 cm^{-1} was observed. The presence of exposed aluminum ions was confirmed by the EPR spectrum of adsorbed NO and O_2^-.

INTRODUCTION

Although at least one reference appears in the patent literature concerning the activity of an AlY zeolite (*1*), no detailed work has been published on this very interesting zeolite. In the present work an attempt was made to study the catalytic activity of AlHY for the disproportionation of toluene. In addition, the physical properties including thermal stability were determined as a function of composition. It was of particular interest to investigate whether the introduction of aluminum ions into cationic positions would produce a zeolite that was similar to the ultrastable zeolite.

The ion exchange phenomena provides some rather unique problems since Al^{3+} hydrolyzes water extensively. Schuster and Fratiello (*2*) have studied aqueous solutions that were approximately 2 *M* in $AlCl_3$ by means of proton magnetic resonance, and their results indicate that the coordination number for Al^{3+} is almost exactly 6 for these solutions. At relatively high concentrations [1 *M* $Al(NO_3)_3$] the pH is about 2, and the aluminum is probably present as $Al(OH_2)_6^{3+}$ and $Al(OH_2)_5OH^{2+}$ because of the reaction

$$Al(OH_2)_6^{+3} + H_2O \rightleftarrows Al(OH_2)_5OH^{+2} + H_3O^+.$$

Dimer species of $Al(OH_2)_5OH^{+2}$ have also been reported by Gruenwald and Fong (*3*) for a pH of 3. In the ion exchange process the proton or hydronium ion is competing with aluminum in its various complex forms. As will be demonstrated, it is possible to obtain zeolites ranging from those in which Na^+ is exchanged mainly with protons to those in which the exchange is primarily with aluminum ions.

EXPERIMENTAL SECTION

The AlHY zeolites were prepared by exchanging the sodium form of a Linde type Y zeolite with aluminum ions and protons in an $Al(NO_3)_3$ solution. During the preparation the concentration of $Al(NO_3)_3$, as well as the different exchange times at 70° and at room temperature, were varied. After the exchange process had been carried out at 70°, and then at room temperature, the samples were washed at least three times with deionized water to remove the nitrate ions. The preparative conditions are listed in Table I. The ultrastable zeolite was prepared according to procedure A described by McDaniel and Maher (*4*). Aerocat AAA (25% Al) was also studied for comparison purposes.

The amount of remaining sodium in the AlHY and ultrastable zeolites was analyzed by treatment of the zeolite with 0.013 *M* $AgNO_3$. The amount of cationic aluminum was analyzed by treatment of the zeolite with 0.1 *N* NaOH, as suggested by Kerr (*5*). The sodium and aluminum content of the resulting solutions were determined by using atomic absorption spectroscopy. The analytical results and the calculated values for the number of sodium ions and cationic aluminum ions per unit cell are shown in Table II. The total molar ratio of SiO_2/Al_2O_3 in AlHY, NH_4Y, and the ultrastable zeolite was obtained by X-ray fluorescence. The total numbers of aluminum ions and lattice aluminum ions are also shown in Table II. These values have an estimated error of 6%.

Based on the analytical results, a unit cell formula is proposed for AlHY zeolites:

$$Na_5H_xAl_y\,[(AlO_4)_{60}(SiO_4)_{136}]\,264H_2O$$

where y = 4 to 16

$$x = 60\text{-}5\text{-}3y$$

assuming all exchangeable aluminum ions have an effective charge of +3. The calculations for AlHY are based on the assumption that the cations present in zeolites are only aluminum ions, protons, and remaining sodium ions. The concentration of protons was obtained by the difference between the original concentration of sodium in a NaY zeolite and the concentration of exchangeable aluminum and remaining sodium ions.

The crystal stability and the dimension of the unit cell were determined by means of an X-ray powder diffraction method. In order to prevent any loss of crystallinity upon exposure to air the zeolites were transferred under vacuum to capillary tubes for X-ray analysis. A Philips X-ray diffractometer with a wavelength of 0.7109 Å was employed.

TABLE I
PREPARATION OF AlHY ZEOLITES

Zeolite	Concentration of $Al(NO_3)_3$ (*M*)	Exchanging time at 70° (hr)	Exchanging time at room temp. (hr)
AlHY-1(A)	1.0	2.0	0
AlHY-1(B)	1.0	2.0	1
AlHY-1(C)	1.0	2.0	2
AlHY-1(D)	1.0	2.0	8
AlHY-1(E)	1.0	2.0	12
AlHY-1(F)	1.0	2.0	18
AlHY-1(G)	1.0	2.0	45
AlHY-1(H)	1.0	2.0	142
AlHY-2(A)	1.0	0.5	0
AlHY-2(B)	1.0	1.0	0
AlHY-2(C)	1.0	1.5	0
AlHY-2(D)	1.0	2.0	0
AlHY-2(E)	1.0	3.0	0
AlHY-2(F)	1.0	4.0	0
AlHY-2(G)	1.0	6.0	0
AlHY-2(H)	1.0	8.0	0
AlHY-2(I)	1.0	12.0	0
AlHY-2(J)	1.0	36.0	0
AlHY-3	0.1	2.0	1

TABLE II

Total Number of Exchanged Aluminum Ions and Lattice Aluminum Ions per Unit Cell

Sample	Silica/Alumina[a] (molar ratio)	Proton content (ions/unit cell)	Exchangeable Al (ions/unit cell)	Total Al[b] (ions/unit cell)	Lattice Al[c] (ions/unit cell)
AlHY-1(B)	4.20	36	4.7	65	60
AlHY-1(D)	4.14	—	—	66	—
AlHY-1(G)	3.89	24	9.0	70	61
AlHY-1(H)	—	3	15.6	—	—
AlHY-2(J)	—	39	3.6	—	—
AlHY-3	3.91	21	9.6	69	59
NaY	—		0.0	—	
NH_4Y	4.95		0.0	55	
ultrastable HY	4.66		9.2	58	

[a] Obtained from analysis by Baroid Division, National Lead Co.

[b] Assuming 136 molecules of silicon per unit cell.

[c] These values were obtained by subtracting exchangeable aluminum from total aluminum values.

The OH groups present on AlHY and decationated Y-type zeolites were studied by means of infrared spectroscopy. The infrared cell was similar to that described by Peri (*6*). The sample was first ground into a powder form and then pressed into a plate which had a size of 1.2 × 2 cm and a surface density of 10–15 mg/cm^2. A Beckman IR 12 spectrophotometer was used to obtain the infrared spectra of the OH groups on AlHY and decationated zeolites after different heating temperatures.

The EPR spectra of NO and the O_2^- species adsorbed on AlHY zeolites were studied by means of a Varian spectrometer (Model 4502). The samples were first broken into small chips and then degassed to 300° or 400° with a heating interval of 100°/hr. After the degassing process, NO was distilled onto the sample from the solid state while the sample was at 23°. The final pressure was either 5 or 20 Torr. The superoxide ion was formed by γ-irradiation of the zeolite in the presence of oxygen. The EPR spectrum was also obtained for an AlHY zeolite which was γ-irradiated under vacuum.

A microcatalytic reactor was used for the studies of the disproportionation of toluene over the catalysts. The catalyst chamber was a stainless-steel tube which had an outside diameter of 0.63 cm and a length of 50 cm. The catalyst bed consisted of 0.25 g of loose catalyst powder. The catalyst was heated to a desired pretreatment temperature by increasing the temperature in 100° increments each hour. The helium flow rate was maintained at 60 ml/min. Reagent grade toluene was injected in the form of 3 μl pulses. Reactions were carried out at a helium flow rate of 25 ml/min. The catalytic activity was also measured after adding 10 μl of deionized water back to the samples after the degassing process. At low conversions, toluene was cleanly disproportionated to benzene and a mixture of the xylene isomers.

The adsorption of toluene on the catalysts was also studied by means of gas chromatography. The samples were preheated to 400° at a helium flow rate of 60 ml/min. The zeolite was then loaded at room temperature by injecting 80 μl of toluene into the helium stream. After the weakly sorbed toluene was removed by flowing He over the sample for 30 min, the temperature was raised continuously to 400°, and the thermal conductivity of the effluent stream was monitored by means of a thermal conductivity cell. The average heating rate was 10°/min. In a related experiment the desorption products were trapped at —196° and subsequently analyzed.

RESULTS

Characterization of AlHY Zeolites

The dimension of the unit cell was determined from the X-ray powder diffraction pattern following dehydration of the zeolites at various temperatures. In Table III results for AlHY-1(H) are compared with the ultrastable zeolite and the original NaY zeolite in the hydrated form. Only a very slight contraction was noted in the unit cell for the AlHY sample relative to the original NaY. This is in marked contrast to the ultrastable zeolite which experienced a 1.3% contraction.

The crystallinity of the zeolites was estimated by visually comparing the higher order reflections, using the ultrastable zeolite as a standard. The AlHY-1(H) sample retained most of its crystallinity even following dehydration at 800°. Upon exposure of this zeolite to water vapor at room temperature following dehydration at 400° no loss in crystallinity was detected. However, exposure of this same sample to water vapor at 400° resulted in a substantial loss in crystallinity. Although these observations are qualitative in nature, one is justified in concluding that the AlHY-1(H) zeolite is not as stable as the ultrastable zeolite to hydrothermal treatment (*4*).

The IR spectra of hydroxyl groups on two AlHY zeolites and a decationated zeolite at different degassing temperatures are shown in Fig. 1. For the proton-rich AlHY-2(J) the spectra reveal two strong bands at frequencies of 3640 and 3540 cm^{-1}. These bands appear for the sample degassed at 300° or 400°, but are less intense at 500°. The same bands were observed for a decationated zeolite degassed up to 500° as reported earlier (*7*). The band at 3740 cm^{-1} appeared in the spectra of AlHY-2(J) when the degassing temperature was only 300°, but for the decationated zeolite it did not appear following dehydration at the lower temperatures. Only very weak hydroxyl bands were observed for the aluminum-rich AlHY-1(H). A band at 3600 cm^{-1}, which was proposed as the characteristic band for ultrastable HY by Jacobs and Uytterhoeven (*8*) and

TABLE III
UNIT CELL DIMENSIONS

Sample	Pretreatment	a(Å)
NaY	—	24.79
AlHY-1(H)	400°	24.75
AlHY-1(H)	800°	24.66
Ultrastable HY-2	400°	24.46

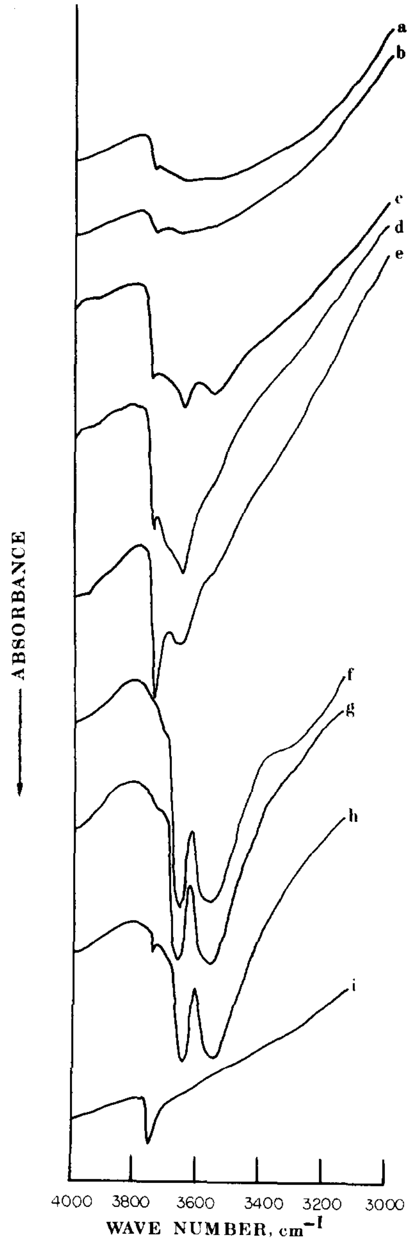


FIG. 1. Infrared spectra of AlHY-1(H): (a) evacuated 1 hr at 300°, (b) evacuated 1 hr at 400°. Infrared spectra of AlHY-2(J): (c) evacuated 1 hr at 300°, (d) evacuated 1 hr at 400°, (e) evacuated 1 hr at 500°. Infrared spectra of NH$_4$Y zeolite: (f) evacuated 1 hr at 300°, (g) evacuated at 1 hr at 400°, (h) evacuated 1 hr at 500°, (i) evacuated 1 hr at 600°.

by Ward (*9*), was never clearly observed either for AlHY or decationated zeolites.

The EPR spectrum shown in Fig. 2a was observed at —196° when NO was adsorbed on several different AlHY zeolites which had been degassed at 300°. The equilibrium pressure of NO at room temperature was 5 Torr. Two high field minima at $g_{\parallel} = 1.95$ and 1.92 were observed. However, only one minimum at $g_{\parallel} = 1.95$ was obtained when the sample was degassed at 400°, as shown in Fig. 2b. When the pressure of NO was increased to 20 Torr, the two appeared again as shown in Fig. 2c. The spectrum of O_2^- on an AlHY has been reported elsewhere (*10*). No correlation was observed between the number of spins and extent of exchange of aluminum. The EPR spectrum of AlHY zeolites irradiated under vacuum, shown in Fig. 3a, exhibited 11 weak hyperfine lines. The relative intensities of these 11 lines are 1:2:3:4:5:6:5:4:3:2:1. A g value of 2.007 and a hyperfine splitting of 10G were obtained. In the presence of 160 Torr O_2 the lines were broadened simultaneously. A similar spectrum, shown in Fig. 3b, was also observed for a γ-irradiated decationated-Y zeolite.

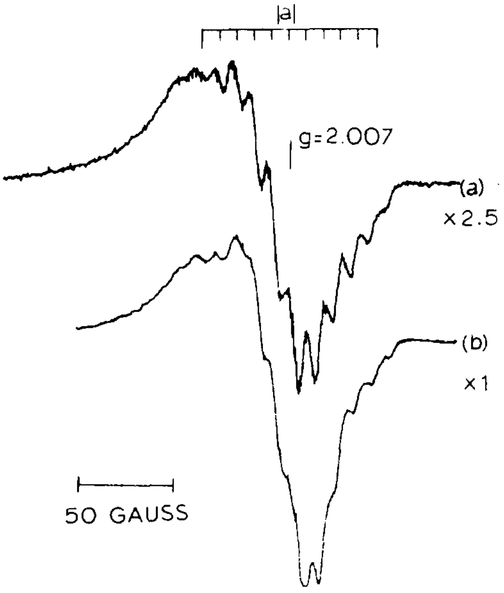


Fig. 3. (a) EPR spectrum of AlHY zeolite irradiated under vacuum, (b) EPR spectrum of decationated-Y zeolite irradiated under vacuum.

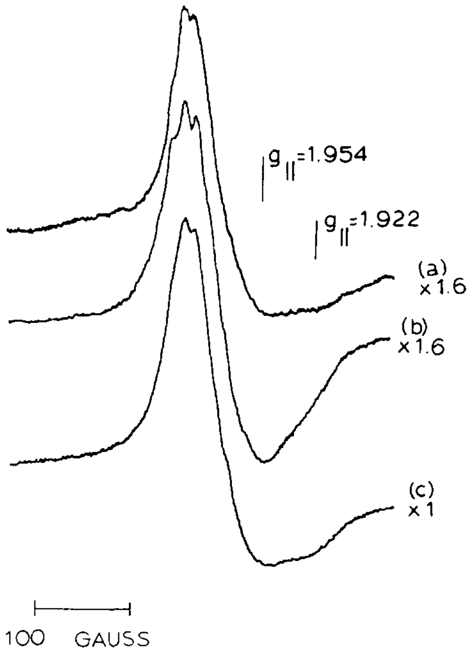


Fig. 2. EPR spectra of NO on AlHY zeolite: (a) degassed at 300°, 5 Torr NO; (b) degassed at 400°, 5 Torr NO; (c) degassed at 400°, 20 Torr NO.

Catalytic Studies

The catalytic activity of the AlHY zeolites was studied primarily as a function of the exchange conditions, and, to a lesser extent, the pretreatment temperatures. It was generally observed, as shown in Fig. 4, that the conversion of successive pulses of toluene over AlHY samples decreased continuously until a certain level of activity was reached. The conversion of the second pulse was about ½ to ⅓ of that for the first pulse. The initial conversion of toluene over the same type of AlHY zeolite was reproducible to ±1.5 mole percent.

Figure 5 depicts the initial conversions of toluene at 400° for AlHY-2 zeolites that had been exchanged at 70° for different periods of time. The initial percentage conversion of toluene increased as the exchange time increased, and then remained constant when the exchange time was longer than 5 hr.

Figure 6 shows the initial conversions of toluene at 400° over AlHY-1 zeolites as a function of exchanging time at room

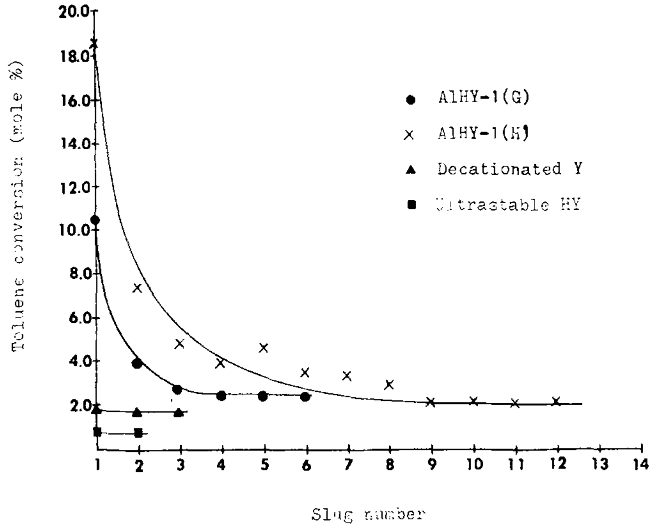


FIG. 4. Catalytic activity of AlHY-1(H) and other zeolites as a function of successive pulses of toluene.

temperature. It was found that the initial conversion increased as the setting time was increased but increased more slowly when the setting time was longer than about 12 hr.

The results also show that the initial conversion of toluene at 400° over AlHY-3 which was prepared in a 0.1 *M* $Al(NO_3)_3$ solution is essentially the same as that of AlHY-1(B) which was prepared in 1 *M* $Al(NO_3)_3$ under the same exchanging conditions. It should be noted from Table II that the amount of exchangeable aluminum was greater in the former case than in the latter.

When the degassing temperature was raised to 500°, the initial conversion of toluene at 400° was decreased to about $\frac{1}{6}$ of that observed for the same catalyst degassed at 400°. The pulse technique was also used to examine effects of the addition of water on the catalytic behavior of AlHY zeolites. It was found that the activity was not increased when water was added to a sample that had been heated at 500° for 1 hr.

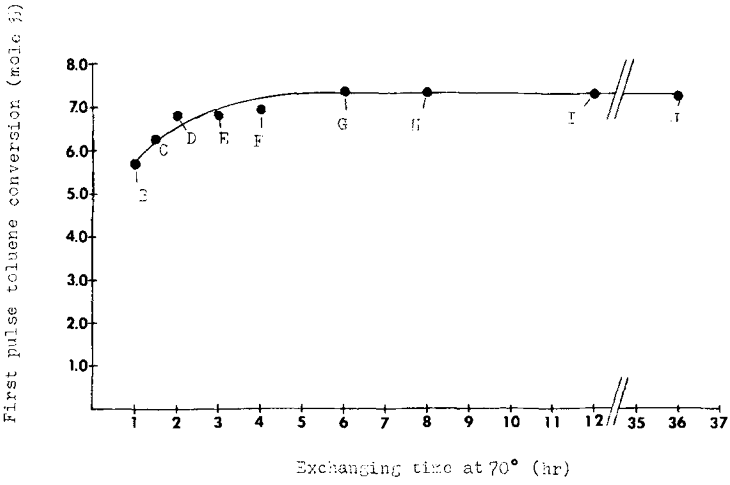


FIG. 5. Plot of catalytic activity (first pulse) over AlHY-2 versus exchanging time at 70°.

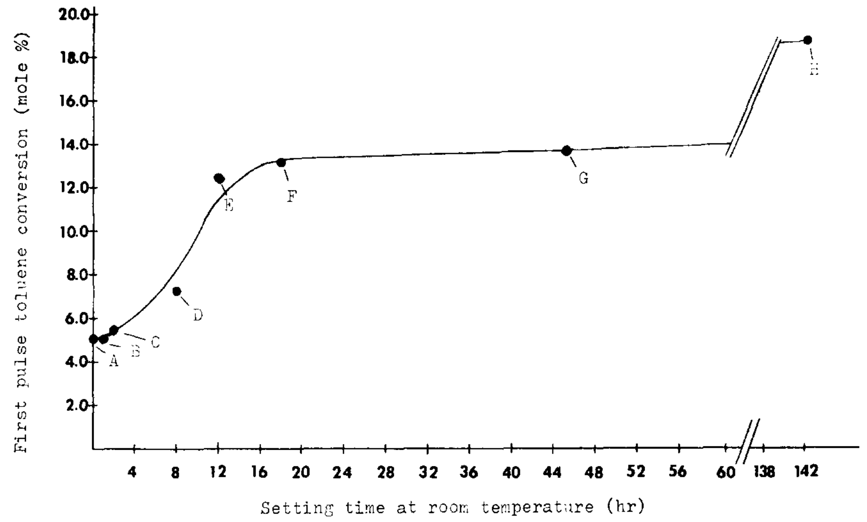


FIG. 6. Plot of catalytic activity (first pulse) over AlHY-1 versus exchanging time at room temperature.

Decationated and ultrastable zeolites are considerably less active than AlHY for the initial pulse; however, the activity of AlHY decays to approximately that of the decationated zeolite, as shown in Fig. 4. The activity of the decationated zeolite was obtained at 400° following dehydration (partial dehydroxylation) at 550°, the dehydration temperature at which decationated zeolites achieve their maximum activity for such reactions. The conversions reported here are in good agreement with the results of Benesi (*11*). Ultrastable zeolites were found to be more active following dehydration at 400°; hence, the catalytic activity reported in Fig. 4 was measured at 400° following dehydration at 400°. Silica–alumina showed no measurable activity under these conditions. A minimum conversion of about 0.1 mole percent could have been detected if a reaction had occurred.

The toluene desorption curves of Fig. 7 show the concentration of desorbed gases in the effluent stream for AlHY, NH_4Y and silica–alumina as a function of the catalyst temperature. The results indicate that under the experimental conditions the total amount of toluene adsorbed on an AlHY zeolite is about the same as the amount adsorbed on a decationated zeolite, and about 2.5 times more than is adsorbed

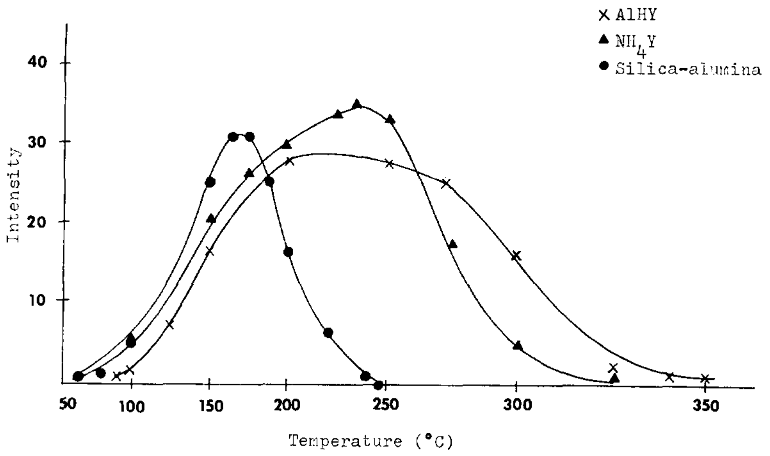


FIG. 7. Toluene desorption curves.

on a silica–alumina sample. More important, when toluene was completely desorbed at 250° for silica–alumina, about half of the total amount of toluene was still adsorbed on an AlHY and a decationated zeolite. The results further show that toluene was held on AlHY to somewhat higher temperatures than on the decationated zeolite. Once the products were frozen in liquid nitrogen, and it was found that only a very small portion of toluene had been converted to benzene.

DISCUSSION

Characterization of AlHY Zeolites

A smaller unit cell dimension was obtained for our ultrastable zeolite compared to the decationated and the NaY zeolite. Kerr (*12*) likewise obtained a lattice contraction of 0.93% when he compared an ultrastable HY with a decationated zeolite, and it is generally accepted that the smaller unit cell is a result of the loss of Al from the lattice. Kerr also reported that up to 25% of the aluminum was present in the cationic form. The results in Table II indicate that about 16% of the aluminum in our ultrastable zeolite was present in the cationic form.

Our results indicate, however, that it is possible to introduce aluminum ions as well as protons into a Y-type zeolite without removing any lattice aluminum. (The data in Table II show an increase in lattice aluminum, but this is probably the result of a small systematic error in the analyses.) The larger size of the unit cell relative to the ultrastable zeolite further supports our conclusion that the lattice aluminum ions are not affected by the low pH. The inhibiting effect of aluminum ions for removal of structural aluminum from clays in strong acids is well known; therefore, it is not surprising that zeolites behave in a similar manner.

Since it is possible to introduce cationic aluminum into a zeolite lattice (in amounts comparable to that found in ultrastable zeolites) without forming an ultrastable zeolite, one may conclude that the presence of cationic aluminum is not *the* critical factor in synthesizing the ultrastable crystal. Removal or replacement of framework aluminum must also be important.

From Fig. 2, it is found that the shape of the NO spectra on AlHY zeolites and the number of spins per gram of sample are affected by the NO pressure and the temperature of dehydration. When 5 Torr of NO was applied, two minima associated with two different adsorption sites were observed at a dehydration temperature of 300°. When the temperature was increased to 400°, the g values and the line shape of the spectrum (Fig. 2b) of NO adsorbed on an AlHY are identical to those observed for NO adsorbed on a decationated-Y type zeolite. This fact indicates that one of the adsorption sites, having $g_{\parallel} = 1.95$ for NO adsorbed on AlHY, is the same site as observed for NO adsorbed on decationated-Y. This site is thought to be a Lewis acid site formed by a tricoordinated aluminum. The other NO adsorption site which corresponds to $g_{\parallel} = 1.92$ probably is associated with the hydroxyl groups which were not completely removed, even when the temperature was raised to 400°. When the NO pressure was increased to 20 Torr, the NO species was first adsorbed on the site with $g_{\parallel} = 1.95$ and then the excess NO gas adsorbed on the less preferred site with $g_{\parallel} = 1.92$ (Fig. 2c).

The eleven-line spectrum, shown in Fig. 3, indicates an unpaired electron trapped between two equivalent aluminum atoms. Since the aluminum atom has a nuclear spin of 5/2, the coupling between two equivalent aluminum atoms will induce $(2)\cdot(5/2) + 1 = 11$ lines with the relative intensities 1:2:3:4:5:6:5:4:3:2:1. The reversible line broadening effect with molecular oxygen indicates that the aluminum ions are exposed to the supercage of the zeolite.

Ion Exchange and Catalytic Studies for AlHY Zeolites

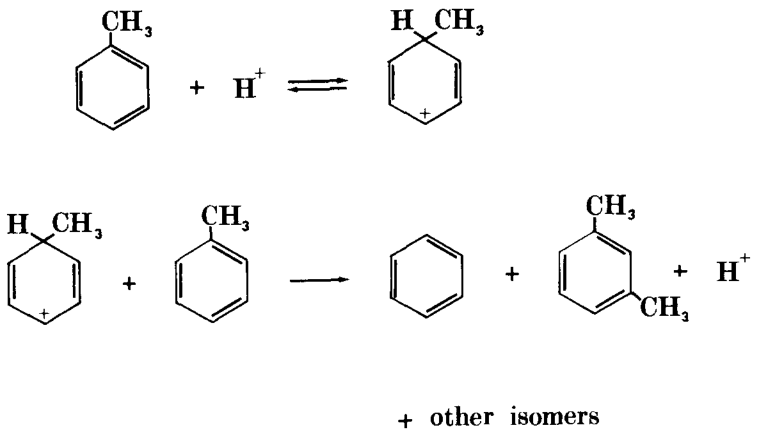
The analytical data shown in Table II implies that proton exchange is favored at the higher temperature and that aluminum ion exchange is favored at the lower temperature. The temperature dependence of the proton and aluminum exchange equilibrium may be explained in terms of an entropy effect, i.e., the entropy change of this complex aluminum exchange reaction is negative. The standard free energy change will become less negative as the temperature is increased; therefore, the aluminum exchange reaction will become less favored.

The catalytic data presented here clearly demonstrated that the AlHY zeolite has an activity for toluene disproportionation that is equal to or greater than the other acidic Y-type zeolites. It is interesting to speculate as to why this activity develops at a much lower dehydration temperature. Hildebrandt and Skala (*13*) have suggested that trace amounts of ammonia remain on the catalyst derived from NH_4Y. This ammonia which poisons the very strong Brönsted acid sites can only be removed by oxidation or by degassing the sample at temperatures higher than 500°. With no ammonia present, one would expect the activity to develop as the strongly acidic sites were formed. The exposed lattice aluminum sites, as determined for the EPR spectra, also developed at a much lower temperature on the AlHY zeolites. This supports our earlier model in which this defect creates strongly acidic sites through an inductive effect on adjacent OH groups (*14*).

The infrared results also confirm an earlier observation that the catalytic activity on acidic zeolites does not correlate with the concentration of hydroxyl groups in either the 3640 or the 3650 cm^{-1} bands (*14*). In the previous case the observation was made with respect to NH_4Y dehydrated at elevated temperatures, and in the present case it is apparent that the activity was greatest for the aluminum-rich sample, whereas the hydroxyl concentration was least for this sample.

At least two reasonable explanations can be offered for the rapid poisoning of the AlHY either by the toluene or the reaction products. One is reminded of the similarity between the results obtained here and those reported by Hall, Lutinski, and Gerberich (*15*) for 2,3-dimethylbutane cracking on γ-Al_2O_3 and silica-alumina. It was observed by these authors that in a similar pulse reactor the γ-Al_2O_3 was more active initially, but that it was poisoned easily and became less active than the silica–alumina. The cationic alumina in the zeolites may be similar to that found at the active sites in γ-Al_2O_3. Alternately, the relative instability of the hydroxyl groups on AlHY suggests that the reaction process may actually dehydroxylate the zeolite or that the protons may be transferred to less acidic sites.

Although the origin of the "superactivity" of acidic zeolites relative to silica–alumina has not been adequately explained, it appears that the concentration of the reactant in the zeolite at high temperatures could be a significant factor, particularly if the reaction proceeds according to the following mechanism:



Here the second reaction is considered to be the slow step and it readily follows that the rate would be second order in the concentration of toluene. Now if one considers the desorption curves in Fig. 7, it is obvious that at 350° the concentration of toluene in the zeolite is much greater than the concentration on silica–alumina. Admittedly, these results were not obtained under the exact reaction conditions; yet, they do demonstrate this one essential property of the zeolite. Bolton and Lanewala (*16*) recently explained the products from hexane isomerization over zeolites in terms of a bimolecular reaction, and they also proposed that the higher activity of these catalysts may be attributed to their unique adsorptive characteristics. Work is currently in progress to quantitatively determine the concentration of the reactant at the exact reaction conditions.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of Drs. P. E. Eberly and J. V. Kennedy in obtaining analyses of the zeolites. This work was supported by the National Science Foundation under Grant GP-19875.

REFERENCES

1. MEYERS, C. G., ROPE, B. W., HILL, M., AND GARWOOD, W. E., U. S. Pat. No. 3,384 572 (1968).

2. SCHUSTER, R. E., AND FRATIELLO, A., *J. Chem. Phys.* **47,** 1554 (1967).

3. GRUENWALD, E., AND FONG, D. W., *J. Phys. Chem.* **73,** 650 (1969).

4. MCDANIEL, C. V., AND MAHER, P. K., "Molecular Sieves," Society of the Chemical Industry, London, 1968, p. 186.

5. KERR, G. T., *J. Phys. Chem.* **71,** 4155 (1967).

6. PERI, J. B., AND HANNAN, R. B., *J. Phys. Chem.* **64,** 1526 (1960).

7. WARD, J. W., *J. Catal.* **9,** 225 (1967).

8. JACOBS, P., AND UYTTERHOEVEN, J. B., *J. Catal.* **22,** 193 (1971).

9. WARD, J. W., preprints, 2nd Int. Conf. Molecular Sieve Zeolites, Worcester, 1970, p. 682.

10. WANG, K. W., AND LUNSFORD, J. H., *J. Phys. Chem.* **75,** 1165 (1971).

11. BENESI, H., *J. Catal.* **8,** 368 (1967).

12. KERR, G. T., *J. Phys. Chem.* **73,** 2780 (1970).

13. HILDEBRANDT, R. A., AND SKALA, H., *J. Catal.* **12,** 61 (1968).

14. LUNSFORD, J. H., *J. Phys. Chem.* **72,** 4163 (1968).

15. HALL, W. K., LUTINSKI, F. E., AND GERBERICH, H. R., *J. Catal.* **3,** 512 (1964).

16. BOLTON, A. P., AND LANEWALA, M. A., *J. Catal.* **18,** 1 (1970).