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The Thermal Behavior of Crystalline Aluminosilicate Catalysts

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The activation of acid-type catalytic properties in sodium, rare-earth sodium, ammonium, and rare-earth ammonium-containing Y-type faujasite catalysts after precalcination has been determined by the isomerization and disproportionation of 1-methyl-2-ethylbenzene and by simultaneous differential thermal and effluent gas analyses. The maximum catalytic activity is associated with a weak dehydration process. The correlation between the temperature of dehydration and optimum precalcination temperature was good.

Activation conditions depended on the cations present in the zeolite. Sodium Y-type faujasite showed no catalytic activity. Rare-earth-containing Y-type zeolite was activated at a lower temperature than the deammoniated Y-type zeolite. When both rare-earth and ammonium ions were simultaneously present in the zeolite, the thermal activation curves had two activity maxima. These occurred at temperatures corresponding to those found for the individual ions alone.

INTRODUCTION

Zeolite catalysts have acidic properties which promote alkylation of aromatics and other Friedel-Crafts-type reactions. Naturally occurring and synthetic zeolites or molecular sieves do not exhibit acidic catalytic activity, however. Activation of the acidic catalytic properties requires at least two steps. First, the alkali metal cations present must be exchanged for reducible, polyvalent, hydrogen, or hydrogen precursor (e.g., ammonium) cations. Second, the ionically exchanged zeolites must be heated to develop the acidic catalytic properties. The hydrogen and rare-earth cation forms of faujasite have proven to be versatile, highly acidic catalysts and have found wide acceptance in petroleum refining operations. Venuto *et al.* (*1*) have reported activation temperature studies on the alkylation of benzene with ethylene using hydrogen Y-type rare-earth X- and rare-earth Y-type faujasite catalysts. The activities are similar, but striking differences in the activation procedures are required to obtain these activities (*1*). Different activation temperatures for zeolite catalysts of similar composition and structure have been reported in the literature (*1–5*) Zeolite catalysts appear to be particularly sensitive to the activation temperature. We wished to explore the problems associated with the activation of zeolite catalysts with a view to devising diagnostic tests for activation and discovering the basis of this interesting phenomenon.

EXPERIMENTAL

Catalysts. Catalysts were prepared from a sample of pure sodium Y-type molecular sieve supplied by the Linde Company. The molecular sieve as received contained 13.0% Na_2O, 63.5% SiO_2, and 23.5% Al_2O_3 on a dry basis. An ammonium Y-type molecular sieve was prepared from this material. Sodium was first completely exchanged for silver by multiple exchange with dilute silver nitrate solutions. The silver was subsequently removed with ammonium thiocyanate as the thiocyanate complex anion. The finished catalyst contained 10.3% $(NH_4)_2O$ and 0.017% Na_2O on a dry basis. A rare-earth sodium catalyst was prepared from the same starting material by multiple exchange with 1 molar mixed rare-earth chloride solutions, washed free of chloride ion and dried at 100°C. This catalyst contained 29.8% rare-earth oxides and 0.62% Na_2O on a dry basis.

A second ammonium-exchanged molecular sieve was prepared by multiple exchange of the sodium Y-type material with dilute ammonium chloride solutions, washed free of chloride and dried at 100°C. The catalyst contained 8.3% $(NH_4)_2O$, 1.62% Na_2O, 23.2% Al_2O_3, and 66.1% SiO_2 on a dry basis. A rare-earth ammonium molecular sieve was then prepared from this material in the same manner used to prepare the rare-earth sodium molecular sieve. The final rare-earth catalyst contained 13.3% cerium oxide, 1.86% lanthanum oxide, and 1.62% Na_2O by analysis.

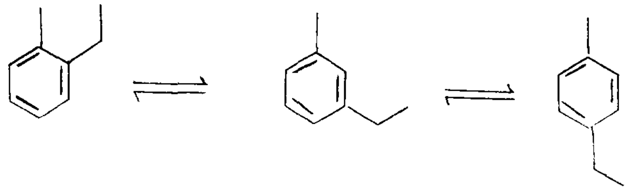
A sample of Linde SK-500 alkylation catalyst was supplied by the Linde Division of the Union Carbide Corporation. This catalyst is proposed for use in the alkylation of aromatic compounds and related Friedel-Crafts reactions. It is a crystalline aluminosilicate derived from type Y molecular sieve. The properties and applications of the catalyst are described in a special report available from the Linde Company (*5*). According to the manufacturer, this catalyst contains 10% rare-earth oxides, 1.62% Na_2O, 22.1% Al_2O_3, and 66.3% SiO_2.

All catalysts were pelleted in a Parr hand-pelleting machine, crushed, and sized to 60-100 mesh prior to testing.

Thermal analysis. Simultaneous differential thermal and effluent gas analyses (DTA/EGA) were made on a thermal analyzer similar in design to the R. L. Stone Company Model LA-XYH Controlled Environment Differential Thermal Analyzer. Differential temperatures are referred to +60–100 mesh alundum. The temperature program rate was 10°C/min. Normal DTA recording sensitivity was 10 μV/inch using a 10% Rh-Pt/Pt differential thermocouple. High-purity tank nitrogen was passed over the sample at 20 ml/min flow rate. EGA analyses were recorded simultaneously with the DTA using a hot tungsten filament catharometer maintained at 150°C. Recording sensitivity was 63 μV/inch. Polarity was chosen to produce a positive recorder response for evolved gases with thermal conductivity greater than that of nitrogen at 150°C. Typical measurements required 75 mg of +60–100 mesh sample. Thermograms are discussed in the indexing conventions of MacKenzie (*6*).

Activity tests. The isomerization of 1-methyl-2-ethylbenzene was used to determine catalytic activities. This reaction is similar to but more sensitive than xylene isomerization (*7, 8, 9*) used extensively in the past for measuring acid activities of heterogeneous catalysts because the ethyl side chain has greater mobility than the methyl side chain in acid-catalyzed reactions. Diethylbenzene isomerization has also been used for catalyst acidity measurements (*10*).

The products of 1-methyl-2-ethylbenzene isomerization are 1-methyl-3- and 4-ethylbenzenes:



Disproportionation to toluene and methyldiethylbenzenes is a significant side reaction. Disproportionation and alkylation reactions have been used to determine the acid activity of rare-earth-exchanged molecular sieves (*1–3, 11, 12*).

One-tenth gram of 60–100 mesh catalyst particles was mixed with an equal volume of 28-mesh alundum and loaded in the center of a 76-cm long, 0.635-cm OD fixed-bed stainless steel tubular reactor. Alundum (28 mesh) was loaded below and above the catalyst charge. A Harvard infusion pump was used for liquid feed delivery. Experimental test conditions were H_2-to-methylethylbenzene molar ratio of 5, atmospheric total pressure, and a liquid hourly space velocity of 5.7. Gaseous reaction effluent samples were taken at the end of 20-min feed periods. The samples were analyzed over a 6.5 m long, 0.475-cm OD silicone elastomer gas chromatographic column.

Catalyst samples were first preheated at 204°C for 16 hr in dry hydrogen. An activity test was made at 204°C. The sample was then heated for 1 hr in dry H_2 at 260°C. This was followed by a second activity test at 204°C. Similar cycles followed, with each preheating treatment 55°C higher than in the preceding test. The final part of each heatup period was programmed slowly to avoid possible self-steaming of the catalyst. Thus, the preheating temperature continuously increased in successive test cycles; but test temperatures remained constant (316°C for the rare-earth sodium sieve, 204°C for the other catalysts).

As the preheating temperature passed 482°C, any accumulated coke was burned off the catalyst samples with a 1:1 nitrogen:air mixture. Coke burnoff temperature was 427°C for the first occasion (after the 482°C preheat cycle) and 482°C on subsequent preheat cycles. Parallel tests showed that coking was moderate, with little effect on catalyst activities.

Results and Discussion

The synthetic molecular sieves or zeolites are crystalline aluminosilicates of the tektosilicate class of minerals possessing high surface areas, regular three-dimensional channel systems, and high cation exchange and gas sorption capacities (*13*). The port size of the faujasite lattice is the largest of the known zeolites. Faujasite is therefore of catalytic interest. Both the sorptive (*14*) and catalytic (*15*) properties of the faujasite lattice can be changed by cation exchange. When the exchanged cation is polyvalent, hydronium ion, or a protonic precursor (e.g., ammonium ion) the aluminosilicate framework acquires acidic properties and can serve as an acid-type catalyst. Based on infrared studies, Uytterhoven, Christner, and Hall (*16*) have proposed an iconic model to describe the acidic features of aluminosilicate catalysts. Recent work (*17, 18*) has contributed to the refinement and extension of this model.

The iconic model of decationized faujasite has been discussed by several authors (*16–19*). Uytterhoven, Christner, and Hall showed that the ammonia is essentially completely removed from ammonium-exchanged Y-type faujasite on heating to 500°C. The liberated proton reacts with lattice oxygen atoms to form hydroxyl groups. The hydroxyl concentration reaches a maximum at 290°C. Secondary dehydration becomes critical between 520° and 590°C. The concentration of the hydroxyl groups remaining depends on the rate of heating. Ward has extended the model to include the acidic behavior of faujasites containing polyvalent ions (*18*). Alkaline earth cations were found to lose hydroxyl groups above 400–500°C. In both the decationized (i.e., deamminated NH_4 faujasites) and polyvalent cation-exchanged faujasites, hydroxyl groups are sources of acidity. In view of the major role of bound water in contributing to the presence of surface OH groups, and thus to the acidic properties of the faujasite lattice, thermal dehydration is expected to play a key role in determining acidic catalytic properties. It will be important to know conditions which develop maximum activity. Dehydration processes are readily detected by thermal analysis. This has proved to be a useful diagnostic test to define optimum thermal activation conditions.

In the DTA/EGA analyses of the sodium Y-type molecular sieve (Fig. 1a), the very strong initial endotherm occurring in the thermogram from ambient temperature to 340°C (with a maximum at about 150°C) is accompanied by water evolution. This is characteristic of molecular sieves (*20*) and high-area polar adsorbants (*21*) and is due to the removal of physically adsorbed water. The very weak exotherm observed at about 940°C is due to the

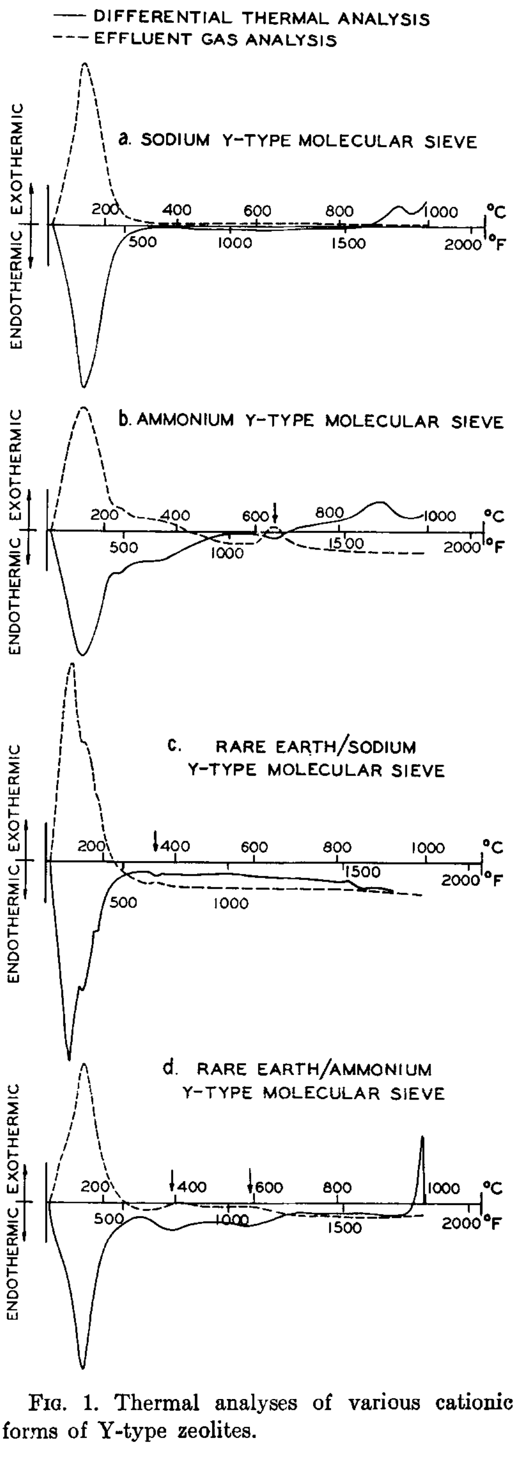


Fig. 1. Thermal analyses of various cationic forms of Y-type zeolites.

collapse of the zeolite framework. No other thermal processes are observed. The sodium Y-type molecular sieve (Na-Y) shows no acid activity when tested for isomerization and disproportionation of 1-methyl-2-ethylbenzene.

The thermal analysis of the ammonium form of the Y-type molecular sieve indicates a maximum rate of desorption of physically adsorbed water between 150–180°C (Fig. 1b). Dehydration and deammoniation continues to about 530°C. Deammoniation of the lattice to produce a hydrated protonic form of the zeolite (HY) occurs stepwise in three stages. Evolution of water and ammonia reaches maxima at 275°, 370°, and 430°C. The zeolite framework collapses at approximately 900°C as indicated by the very weak* endotherm between 840° and 960°C. An additional very weak endothermic dehydration process occurs between 600° and 720°C (arrow in Fig. 1b). The endotherm is associated with the critical dehydration of the deammoniated Y-type zeolite lattice as described by Uytterhoven, Christner, and Hall (*16*). Hughes and White (*17*) report infrared studies of chemisorbed organic nitrogen bases on Y-type faujasites. These authors show the rapid decrease of acid sites above 600°C. Ward (*18*) also detected the endothermic dehydration (accompanied with the decrease of acid sites) in flowing helium between 600° and 720°C. Venuto, Wu, and Cattanach (*22*) and McDaniel and Maher (*23*) detected by DTA a very weak endothermic process near these temperatures on Y-type molecular sieves. The infrared and thermoanalytical data clearly indicate that the dehydration of a deammoniated Y-type molecular sieve between 600° and 700°C affects the acid sites.

The completely deammoniated Y-type molecular sieve (HY) catalyst was the most active catalyst tested for the isomerization and disproportionation of 1-methyl-2-ethylbenzene. For this catalyst, the isomerization activity increased sharply after heating at 427°C (Fig. 2). Maximum activity was reached after the catalyst was heated between 600° and 650°C. Activity fell rapidly above 700°C. However, some activity was retained even after 1 hr cal-

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* "Very weak" defined according to the convention of MacKenzie (*6*).

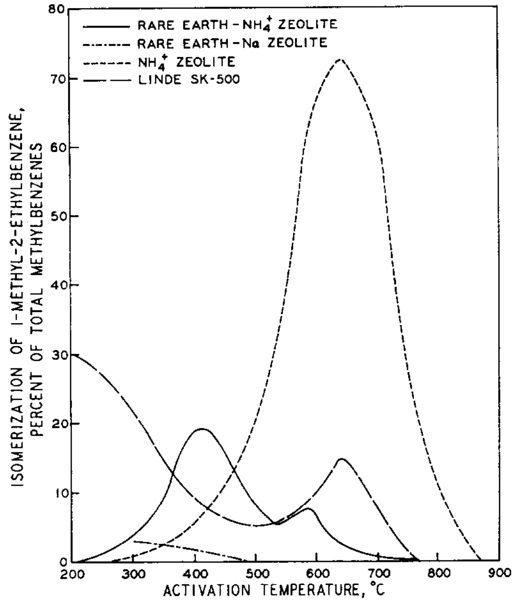

FIG. 2. Thermal activation curves for zeolite catalysts; isomerization of 1-methyl-2-ethylbenzene.

cination at 870°C. These temperatures of precalcination for developing acid activity agree with those reported by Venuto *et al.* (*1*) for developing activity for the alkylation of benzene with ethylene using a similar (HY) catalyst. The temperature range of precalcination in which maximum activity was achieved was identical to the range in which the catalyst underwent a very weak endothermic dehydration as detected by thermal analysis. These data suggest the dehydration process is associated with activation of the catalyst. Similar conclusions apply to the activation of disproportionation activity (Fig. 3).

The thermal analysis of the rare-earth sodium (RE NaY) zeolite shows the characteristic lattice hydration due to the removal of physically held water below 300°C. This is followed by a very weak endothermic dehydration of the zeolite between 330° and 360°C (arrow Fig. 1c). As this catalyst contains no ammonium ions, this dehydration is associated either with "strongly" held physisorbed water or with the hydrated cations of the zeolite. Infrared studies by many workers have established that water may be retained by molecular sieves as hydroxyl groups associated with the cations (*18*, *24–27*). Carter, Lucchesi, and Yates (*24*) showed X-type faujasites contain hydroxyl groups which remain after heating to 450°C. Ward (*18*) has inferred from infrared pyridine adsorption measurements that divalent cations retain hydroxyl groups below 400–500°C. Further, hydrated divalent cations may dissociate to form the conjugate protonic acid and base. Rabo *et al.* (*27*) have reported infrared absorption data on cerium- and calcium-exchanged Y-type faujasite that show these zeolites are dehydroxylated between 500° and 700°C. Smith, Bennett, and Flanigen's (*28*) X-ray data suggest lanthanum ions may be stabilized by water and hydroxyl groups within the faujasite framework. The lanthanum ions occupy different lattice positions depending on the state of hydration. Thus, structural changes may be anticipated on heating rare-earth Y-type faujasite above 180–200°C. The X-ray diffraction, infrared, and thermal analytical data suggest polyvalent cations within the zeolite are hydrated and can promote acidic behavior.

The precalcination temperature of maximum activity observed for the rare-earth

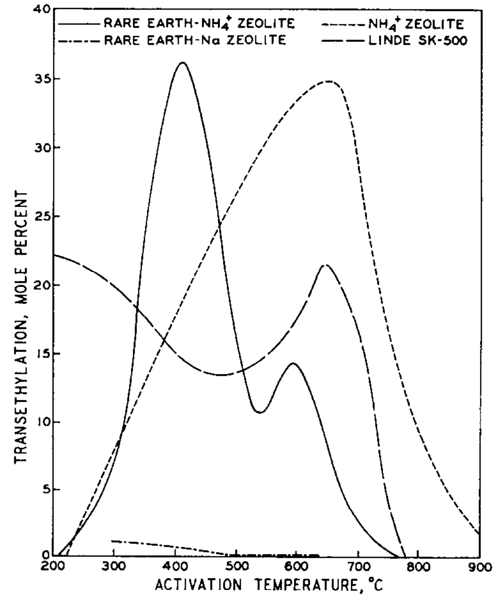

FIG. 3. Thermal activation curves for zeolite catalysts; transethylation of 1-methyl-2-ethylbenzene.

sodium Y-type molecular sieve (RE NaY) was below 310°C. No activity was observed above a precalcination temperature of 480°C (Figs. 2 and 3). Venuto *et al.* (*1*) report catalytic activation of a rare-earth-containing Y-type zeolite between 200° and 300°C. The temperature interval of catalytic activation is the same as that in which a very weak endothermic dehydration was observed in our thermal analytical experiments. This suggests a dehydration associated with the rare-earth cations of the lattice. This dehydration might be related to the activation of the acidic catalytic properties.

Four thermal processes are observed in the thermogram of the rare-earth ammonium (RE NH_4Y) zeolite (Fig. 1d). Two very weak broad endothermic dehydration processes are bracketed between the very strong endotherm due to the desorption of physically held water (between ambient temperature and 300°C) and the sharp medium exotherm associated with the collapse of the structure (between 940° and 1000°C). The low-temperature very weak dehydration (between 300° and 470°C) occurs in the same temperature range observed for the rare-earth-activated catalyst (RE NaY). The high-temperature very weak endothermic dehydration (between 520° and 700°C) occurs in the same temperature range observed for the deammoniated catalyst. Two separate and distinct dehydration processes associated with each of the different cations in the faujasite lattice are observed rather than an "averaged" effect. This suggests separate ionic sites are involved.

When Y-type molecular sieve contained both rare-earth and ammonium ions, *two* catalytic activity maxima were observed. These occur after preheating at 410° and 585°C (Figs. 2 and 3). The high-temperature maximum in the activity occurred at the optimum preheat temperature found for the HY catalyst. The lower temperature agrees with the optimum temperature found for the RE NaY catalyst. Each temperature agrees with the temperature associated with a dehydration detected by thermal analysis. Two types of acid sites are indicated: one is associated with the rare-earth cations, the other with the "deammoniated" (hydronium) sites. The sites are distinct and independent. Rare-earth ion sites activate at a lower temperature than hydronium sites.

Double maxima in the precalcination temperature activity curve for Linde SK-500 alkylation catalyst were also observed to occur at 260° and 650°C (Figs. 2 and 3). These temperatures are in agreement with the results of this work and of Venuto *et al.* (*1*).

SUMMARY

The activation of acid-type catalytic properties on heating rare-earth and ammonium-exchanged Y-type molecular sieves occurs over rather narrow precalcination temperature intervals. These zeolite catalysts exhibit a weak endothermic dehydration at these temperatures. The correlation between the optimum temperature of precalcination to develop the maximum catalytic activity as measured by the isomerization and disproportionation reactions of 1-methyl-2-ethylbenzene and the peak temperature for the dehydration process as measured by thermal analysis is very good. The optimum temperature of precalcination depends on the cation present in the zeolite. When both rare-earth and ammonium ions are simultaneously present, two activation temperatures corresponding to those found for the individual cations are observed. Thus, each cation creates distinct and independent acid sites within the zeolite lattice.

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