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Relationship between Catalytic Activity and Nature of Acidity of the Crystalline Zeolites, Mordenite and Y Faujasite

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Reactions of toluene, *n*-butane, and *n*-pentane catalyzed by two crystalline zeolites, mordenite and Y faujasite, have been determined as a function of the extent of decomposition of the ammonium zeolites to their hydrogen (Brönsted acid) and hydrogen-free (Lewis acid) forms. Removal of the water of constitution from the hydrogen forms destroys their catalytic activity; readdition of water restores activity. The hydrogen ions released upon decomposition of the ammonium forms of these zeolites therefore appear to be the seat of catalytic activity.

The seat of catalytic activity in solid aluminosilicates has been the subject of considerable study and speculation. Although most investigators agree that highly acidic sites on such solids are the seat of catalytic activity, the question most often raised (*1–4*) is whether such sites consist of strong hydrogen (Brönsted) acids or of more generalized (Lewis) acids such as incompletely coordinated aluminum ions. This question is difficult to resolve partly because of the close similarity between Lewis and Brönsted acids in their reactions with electron donors, and partly because both types of acid are present on aluminosilicate surfaces (*4–8*). In the case of the amorphous aluminosilicates used as cracking catalysts, the above question is especially difficult to resolve because only a small fraction of the hydrogen atoms in this type of solid appears to be strongly acidic. Most of the hydrogen atoms appear to be present as hydroxyl groups arising from uncombined silica (*9, 10*).

The two crystalline zeolites, mordenite and Y faujasite, do not suffer from the drawback just mentioned. The lattices of both solids are made up of a porous network of AlO_4 and SiO_4 tetrahedra (*11, 12*); no uncombined silica or alumina is present in the pure compounds. With the exception of a relatively small number of hydroxyl groups arising from trace impurities (*13*) or present on the external crystal surfaces (*8*), all the hydrogen atoms in the hydrogen (Brönsted acid) form of this class of aluminosilicates should be highly acidic provided the crystal lattice remains intact. The synthetic mordenite and Y faujasite used in the present work appear to fulfill these requirements. Furthermore, their hydrogen forms can be converted to the hydrogen-free (Lewis acid) forms (see following sections) without attendant destruction of the zeolite lattice. These two zeolites are therefore ideal subjects for the study of the relationship between catalytic activity and the nature of surface acidity.

Our experimental work consisted of two steps: thermogravimetric analysis of the evolution of water and ammonia from the ammonium forms of mordenite and Y faujasite, and the parallel determination of the catalytic activity of the zeolite products for reactions of toluene, *n*-butane, and *n*-pentane. Comparison of the two sets of results enabled the determination of catalytic activity as a function of chemical composition for the two zeolites under study.

EXPERIMENTAL DETAILS

Materials. The ammonium forms of mordenite and Y faujasite used in the present study were prepared from the respective sodium forms. The sodium form of synthetic mordenite was obtained from Norton Company with the designation, Na-Zeolon (ultrapure powder). It was converted to the ammonium form by repeated equilibrium with fresh portions of 0.2 *M* ammonium nitrate until flame tests of the filtrate showed only trace amounts of sodium present. Analysis of the product dried at 120°C showed that it had the following chemical composition: 3.0 wt % NH_3, 4.6 wt % Al, 35.2 wt % Si, <0.01 wt % Na.

The sodium form of synthetic Y faujasite was obtained from Linde Company with the designation, SK-40 Molecular Sieve Type Y. The sodium ion in this material could not be completely replaced with ammonium ion as in the case of mordenite. Successive washings of the Y faujasite with boiling 1 *M* ammonium nitrate until flame tests of the filtrate showed only trace amounts of sodium resulted in a product that had the following chemical composition after it was dried at 120°C: 5.2 wt % NH_3, 8.5 wt % Al, 23.1 wt % Si, and 0.8 wt % Na. Sodium has been omitted from the empirical formula listed below for Y faujasite.

Thermogravimetric measurements. Thermogravimetric measurements were carried out by means of a Cahn RG electrobalance. The weight of a 0.5-g sample of ammonium zeolite was continuously recorded while the sample was swept with a stream of helium dried over Linde 4A Molecular Sieve. The temperature was raised in 100°C steps; the sample was heated 30 min at each temperature. The temperature range over which ammonia evolution occurred was determined by testing the emerging helium stream with moist litmus paper. Analysis of the completely decomposed zeolite samples showed that all the ammonium ion had indeed been removed during each of the thermogravimetric determinations.

Catalytic activity measurements. The use of the pulse reactor to measure catalytic activity has been previously described by Kokes *et al.* (*14*). In the present study the reactor section consisted of a vertical 12-inch length of stainless steel tubing ¼ inch in diameter. This section formed part of the helium line that led directly to the gas-liquid chromatographic (GLC) unit. The catalyst bed consisted of 0.25 g of zeolite powder diluted with enough inert quartz powder to form a volume of 2 cc. Injection ports were located at the entrance and exit of the reactor tube to allow comparative analyses of 50 μmole hydrocarbon pulses before and after catalytic reaction took place. Reactions were carried out at 400°C and at a helium flow rate of 25 cc/min.

It was found that the conversion of successive pulses of hydrocarbon over the catalyst sample was reproducible to ±0.5 wt %. No appreciable decline in catalytic activity occurred during a given series of tests despite the fact that small amounts of coke were found on the catalyst samples after they were used. Such coke could be burned to carbon dioxide and water by subsequent injection of oxygen pulses.

The GLC column consisted of a 20-ft length of ¼-inch tubing filled with 20 wt % Ucon polar liquid on firebrick. The column was kept at 35°C to analyze products from *n*-butane or *n*-pentane, and was kept at 170°C in the case of the analysis of toluene products.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

The thermogravimetric decompositions of the ammonium forms of mordenite and Y faujasite are shown in Figs. 1 and 2. The temperatures at which ammonia was detected in the exit stream are shown, as are the percentages of ammonia and water calculated from the chemical compositions of the starting materials. These data show that physically sorbed water, ammonia, and water of constitution are evolved in successive stages, though such stages are not always clearly separable. In the case of each zeolite, ammonia evolution begins before all the physically sorbed water is re-

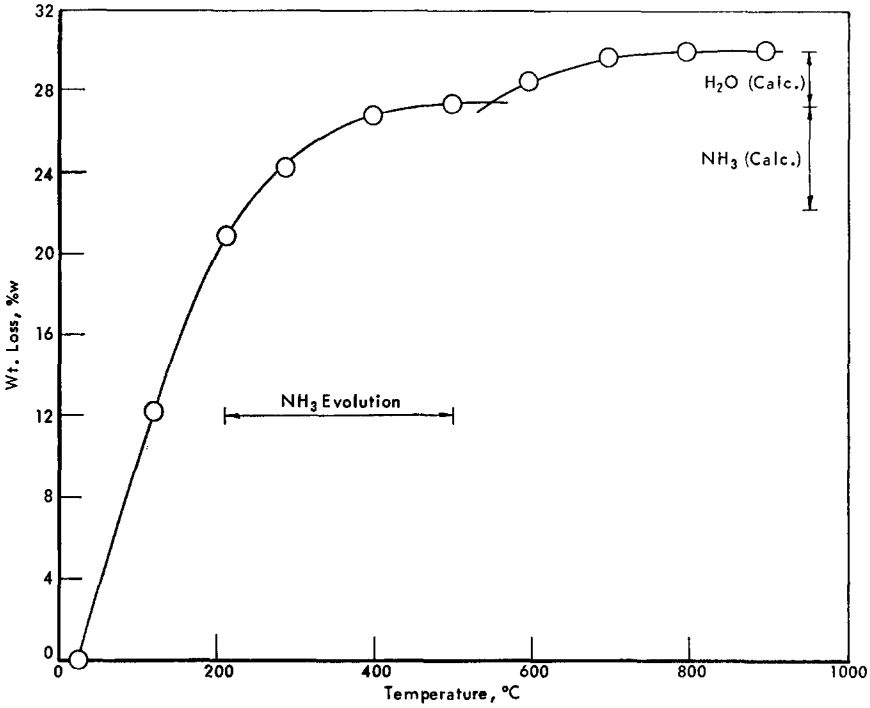

FIG. 1. Thermogravimetric decomposition of Y faujasite (NH_4^+ form).

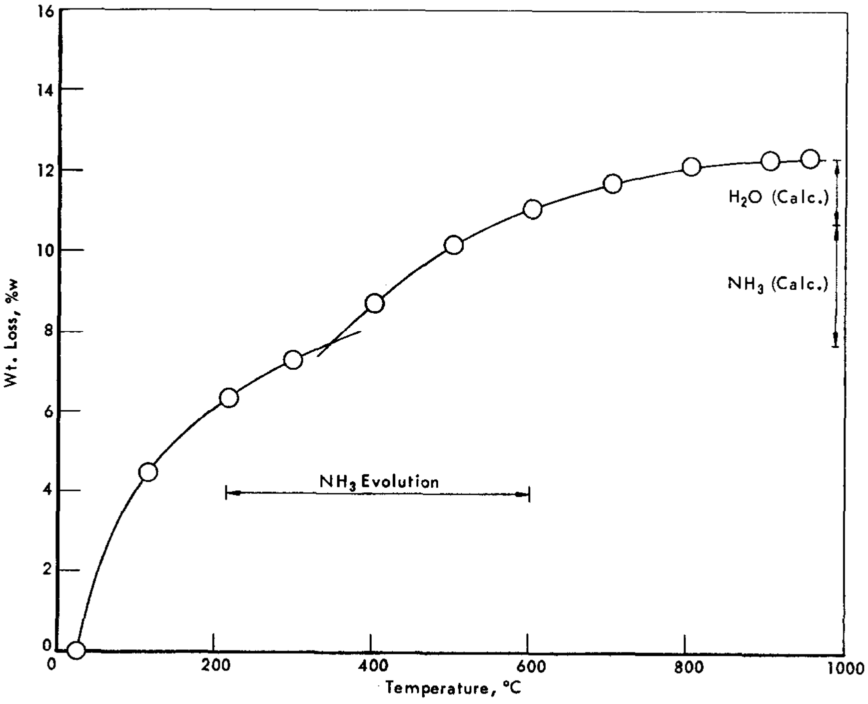

FIG. 2. Thermogravimetric decomposition of mordenite (NH_4^+ form).

moved. It is concluded that the ammonium ion has been completely decomposed to ammonia and residual hydrogen ions at the temperature immediately above that at which ammonia is last detected (600°C for mordenite; 500°C for Y faujasite). At this stage of decomposition, the approximate empirical formulas for what we denote as the hydrogen (Brönsted acid) forms of mordenite and Y faujasite are $HAlSi_7O_{16}$ and $H_2Al_2Si_5O_{14}$, respectively.

The final step in the thermal decomposition is the removal of hydrogen ion as water from the above hydrogen forms. This step occurs upon raising the temperature from 600° to 900°C in the case of mordenite and from 500° to 800°C in the case of Y faujasite. The fact that a higher temperature is required to remove ammonia in the case of mordenite indicates that this zeolite is more strongly acidic than Y faujasite. The empirical formulas for the resulting hydrogen-free (Lewis acid) forms of mordenite and Y faujasite are $Al_2Si_{14}O_{31}$ and $Al_2Si_5O_{13}$, respectively.

The above results obtained in the case of Y faujasite parallel those reported by Uytterhoeven *et al.* (*8*). The approximate temperature range they report for the two-step decomposition is somewhat lower than that observed in the present study. This difference can be attributed to the fact that decomposition was carried out *in vacuo* in the case of the former study rather than in flowing helium as in the present case.

The picture we propose for the state of the hydrogen atoms in the hydrogen form of the two zeolites under study is different from that proposed by Uytterhoeven *et al.* for Y faujasite. Their infrared measurements of the hydrogen form of Y faujasite show the presence of a new OH stretching band at 3669 cm^{-1}. Since they attribute the new band to vibrations of slightly perturbed SiOH groups, they conclude that a Brönsted acid such as that shown on the left side of Eq. (2) in their paper is not present in substantial quantity in the hydrogen form of Y faujasite. However, we suggest that the 3660-cm^{-1} band could in itself be considered concrete evidence for the existence of just such an acid. The relatively high frequency of the OH vibration would indicate that the OH group is not hydrogen-bonded; i.e., at any instant the hydrogen ion is associated with one oxide ion only.

Catalytic Activity

The catalytic activity of mordenite and Y faujasite for reaction of hydrocarbons at 400°C was measured by means of a pulse reactor after the zeolite had been given pretreatments that closely paralleled the conditions used in the thermogravimetric measurements. The relatively unreactive molecule, toluene, was chosen as the principal reactant because of the hyperactivity of zeolite catalysts, particularly that of mordenite, for hydrocarbon reactions such as the cracking of higher paraffins (*15, 16*). At low conversions, toluene was cleanly disproportionated to benzene and an equilibrium mixture of the xylene isomers over the two zeolites used. At high conversions, appreciable amounts of trimethylbenzene isomers were also formed. On the other hand, *n*-butane and *n*-pentane underwent isomerization and cracking over mordenite at 400°C. These paraffins did not react over Y faujasite at this temperature.

Figure 3 shows conversions of toluene at 400°C over the ammonium forms of mordenite and Y faujasite as a function of zeolite decomposition temperature. It is evident that mordenite is more active than Y faujasite for toluene disproportionation at all stages of zeolite decomposition. The fact that maximum activity is attained in both cases when the zeolite is heated directly beyond the temperature at which ammonia evolution was last obeserved is a strong indication that it is the hydrogen form that is catalytically active. The drop in conversion that occurs in the case of each zeolite when hydrogen ions are removed as water show that the hydrogen-free form is inactive. We thus conclude that Brönsted rather than Lewis acids are the seat of activity for toluene disproportionation in the two zeolites under study.

The above behavior is parallel to that obtained in the case of reactions of *n*-butane and *n*-pentane over mordenite (Fig. 4 and Table 1). Here, too, it is evident that

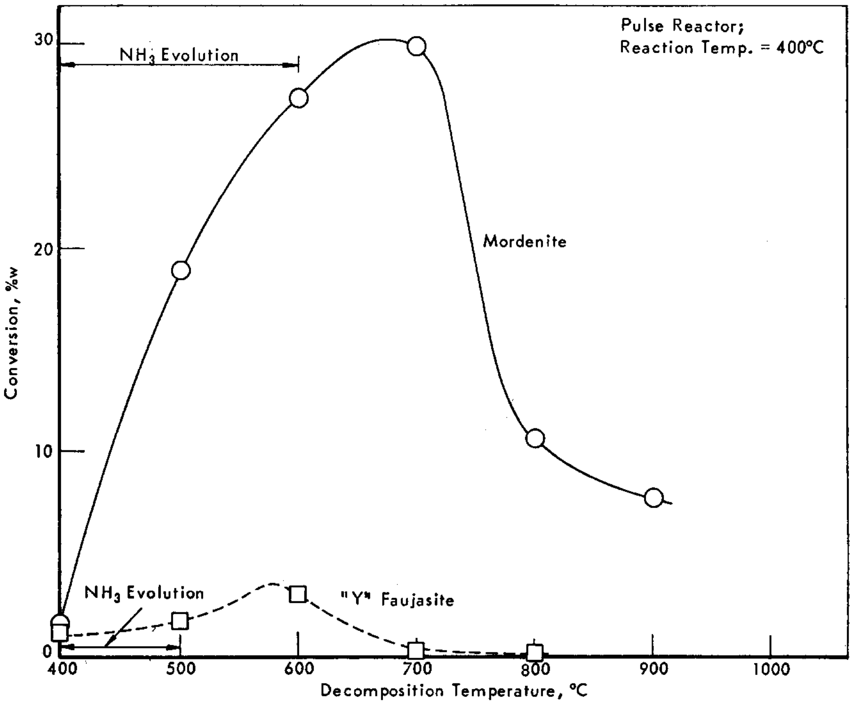

FIG. 3. Disproportionation of toluene over zeolites (NH_4^+ form) vs. decomposition temperature.

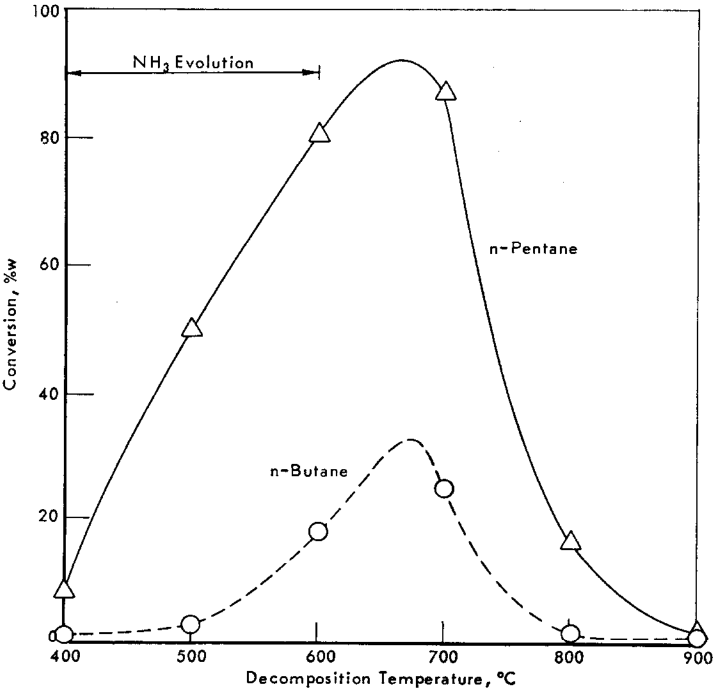

FIG. 4. Reaction of *n*-paraffins over mordenite (NH_4^+ form) vs. decomposition temperature.

TABLE 1

REACTION OF PARAFFINS OVER MORDENITE AT 400°C: EFFECT OF MORDENITE DECOMPOSITION TEMPERATURE

	Decomposition temperature, (°C)	Paraffin conversion, (wt %)	Product composition[a] (wt %)						
			C_1-C_2	C_3	i-C_4	n-C_4	i-C_5's	n-C_5	C_6's
n-Butane	400°	1.0	0.4	0.1	0.5	99.0	0.0	0.0	0.0
	500°	3.1	0.4	0.9	1.6	96.9	0.1	0.1	0.0
	600°	17.2	1.1	9.5	5.4	82.8	0.8	0.4	0.0
	700°	24.8	3.6	15.8	4.0	75.2	0.9	0.5	0.0
	800°	1.6	0.2	0.3	1.0	98.4	0.1	0.0	0.0
	900°	0.3	0.1	0.0	0.2	99.7	0.0	0.0	0.0
n-Pentane	400°	8.9	0.6	0.7	2.1	1.2	2.4	91.1	0.0
	500°	49.5	0.9	22.6	10.1	10.4	5.2	50.5	0.3
	600°	80.3	1.9	42.2	15.1	15.4	5.4	19.7	0.4
	700°	88.4	9.3	14.4	16.5	17.4	3.5	11.6	0.3
	800°	15.8	1.3	4.4	5.7	2.5	1.8	84.2	0.0
	900°	1.8	0.5	0.3	0.8	0.1	0.1	98.2	0.0

[a] All products are paraffins; no olefins are formed.

it is the hydrogen form of mordenite that is active for such reactions. Conversion of n-butane or n-pentane over Y faujasite was negligible at 400°C for all stages of zeolite decomposition shown in Fig. 1.

The pulse technique was also used to examine effects of the addition of water and ammonia on the catalytic behavior of mordenite. Table 2 shows that conversion of n-butane at 400°C is high after decomposition of the ammonium form at 700°C, then drops after decomposition of the hydrogen form at 800°C. However, subsequent addition of water to the hydrogen-free product completely restores its original activity. Thus the hydrogen and hydrogen-free forms of mordenite appear to be interconvertable. It also seems likely that the lattice of mordenite is not damaged upon removal of water at 800°C, a conclusion consistent with the observation that the X-ray diffraction pattern of mordenite is unaltered by any of these treatments. Table 2 also shows that subsequent addition of ammonia poisons catalytic activity. Since the amount of ammonia (80 μmoles) required to poison the activity of the mordenite sample is much smaller than that evolved during decomposition of the original ammonium form (440 μmoles), it is likely that the most active sites have been preferentially neutralized by the ammonia addition.

TABLE 2

REACTION OF n-BUTANE OVER MORDENITE AT 400°C: EFFECT OF WATER AND AMMONIA

Pretreatment	n-Butane conversion, (wt %)	Composition, (wt %)		
		C_1-C_3	i-C_4	C_5's
1/2 hr at 700°C	39.6	29.6	8.1	1.8
1/2 hr at 800°C	2.6	1.2	1.2	0.1
H_2O addition (10 μl)	38.5	24.5	11.3	2.6
1st NH_3 addition (1 cc)	6.8	2.6	3.5	0.7
2nd NH_3 addition (1 cc)	0.3	0.1	0.2	0.0

TABLE 3

DISPROPORTIONATION OF TOLUENE OVER Y FAUJASITE AT 400°C: EFFECT OF WATER[a]

Pretreatment	Toluene conversion, (%)
1/2 hr at 600°C	2.2
1/2 hr at 700°C	0.1
H_2O addition (10μl)	1.5

[a] 50 μmole pulses; 25 cc of He/min.

A similar enhancement of catalytic activity is observed when water is added to the hydrogen-free (Lewis acid) form of Y faujasite. Table 3 shows that most of the initial activity of this zeolite for the disproportionation of toluene to benzene and xylenes is regained when water is added back to the sample that has been decomposed at 700°C.

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