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Reactions of Methylpropene-2-^{13}C on H–Mordenite

III. Effect of Catalyst Pretreatment

FRANÇOIS FAJULA AND FRANÇOIS G. GAULT[1]

Laboratoire de Catalyse, Université Louis Pasteur de Strasbourg, 4 rue Blaise Pascal,
67000 Strasbourg, France

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Reactions of 2-methylpropene-2-^{13}C have been carried out at 120°C on a series of deammoniated mordenite samples activated at various temperatures (120 to 780°C). Although each reaction product had the same characteristic labeling as H–mordenite, significant changes in product distributions have been observed when increasing the activation temperature. Trimethylpentenes (TMP), obtained by cationic dimerization, are formed on ammonium mordenite and their amounts increase only by a factor of 1.5 on zeolites activated at 450°C. At activation temperatures T_a ranging from 450 to 800°C, the decrease in production of TMP parallels closely the decrease in proton concentration, as determined by NaCl ion exchange titration. The amounts of dimethylhexenes, C_5–C_7 hydrocarbons, and hydrocarbon residues increase sharply by a factor of 4 at activation temperatures of 350–400°C, then reach a flat maximum and drop rapidly above T_a = 500°C. The observed increase in activity is interpreted by the generation at 400°C of Lewis sites, allowing formation of a hydrocarbon chain attached to the zeolite framework, and it is suggested that structural changes in the zeolite, arising during the first stages of ultrastabilization, account for the rapid drop of activity beyond 500°C.

INTRODUCTION

The catalytic reactions of methylpropene-2-^{13}C on H–mordenite, investigated under various experimental conditions, generally yield a complex mixture of products in which very often a complete randomization of all the carbon atoms has occurred (*1*). In one case, however, at 120°C on an aged mordenite, a relatively simple product distribution was obtained including selectively labeled dimers (trimethylpentenes and dimethylhexenes) and C_5–C_7 hydrocarbons in which four carbon atoms retain the configuration of the reacting molecule and the additional ones derive from a completely scrambled C_4 unit. It was suggested that these three classes of products, obviously formed according to different reaction mechanisms, were obtained on different types of sites, differing in the strength of their acidity or their location in the mordenite, or both.

To ascertain the nature of these sites, reactions of 2-methylpropene-2-^{13}C have been investigated on a series of H–mordenites which were all derived from the same ammonium form and which were activated at various temperatures.

EXPERIMENTAL

The catalysts were prepared by calcination of an ammonium mordenite (MNH_4; Linde Division, Union Carbide) of the following composition:

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[1] Deceased, August 4, 1979.

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Al_2O_3: 7.1%, SiO_2: 77.1%, Na_2O: 0.03%,
$(NH_4)_2O$: 3.3%, H_2O: 12.5%, SiO_2/Al_2O_3: 10.85.

The reactor used to treat 5 g of ammonium mordenite (0.3 m long, 14 mm in diameter) allowed the air purge (15 ml/min) to pass over the catalyst bed. Such an arrangement was proposed by Weeks *et al.* (*2*) to avoid the exothermic oxidation of ammonia which occurs when the air purge passes through the catalyst bed. During the treatment, the catalysts were first dehydrated for 2 h at 220°C. The temperature was then raised monotonically (7°C/min) to the desired activation temperature (T_a) and kept there for 2 h. After activation, the samples were cooled in an air flow and stored at room temperature. In the following, we will write $MNH_4(500)$, for example, to mean a sample of MNH_4 activated at 500°C.

Before each run, the catalyst (100 mg) was outgassed for 2 h at the reaction temperature (120°C) in a flow of purified hydrogen. The flow system, the experimental procedures, and the analytical methods used have already been described in Part I (*1a*).

For each catalyst, the extent of deammoniation was determined by infrared (ir) spectroscopy, using the N–H stretching band at 1445 cm^{-1}. The spectra were recorded at room temperature with a Perkin–Elmer 457 ir spectrometer. Samples were prepared by pressing a suspension of zeolite in Fluorolub between two disks of potassium bromide.

RESULTS

Gaseous Products and Hydrocarbon Residues

The reactions of isobutene at 120°C have been investigated on nine catalysts obtained from the same NH_4 mordenite by activation at various temperatures from 120 to 780°C. In each case, hydrocarbon residues were formed in an initial stage. After "stabilization" of the mordenite, when the deposition of residues had stopped, the reaction mixture, consisting mainly of olefins (94–99%), was collected, hydrogenated, and analysed. The product distributions are reported in Table 1, together with the conversion α and the amounts of residues formed during the aging period. Figures 1 and 2 show the amounts of residues and the amounts of C_5–C_7 hydrocarbons, dimethylhexenes (DMH), and trimethylpentenes (TMP), all plotted vs the activation temperatures (T_a). The amount of each product, expressed as a percentage of the reaction mixture, was obtained by multiplying the conversion by the percentage in Table 1.

When the activation temperature was increased, two types of variations were distinguishable (Figs. 1 and 2). On the one hand the amounts of hydrocarbon residues, C_5–C_7 hydrocarbons, and dimethylhexenes increased sharply, by a factor of 3–4, at T_a = 350–400°C, then reached a flat maximum, and above T_a = 450°C dropped rapidly to steady values. On the other hand, trimethylpentenes, the major reaction products on MNH_4, also increased at T_a = 450°C, but by a factor of only 1.5, and then decreased slowly at activation temperatures above 500°C.

The variations of the conversion, α, which is the sum of the amounts of C_5–C_7, TMP, and DMH, are represented in Fig. 3. After a sharp increase at 400°C and a pronounced maximum at 450°C, α dropped, first rapidly and then slowly, with increasing activation temperature.

Although hydrocarbon residues, C_5–C_7 products, and dimethylhexenes seem to run parallel in Figs. 1 and 2, slight differences are detectable in their variations with activation temperature. First, the flat maximum for the C_5–C_7 products (Fig. 2) is shifted to the right by 50°C for dimethylhex-

TABLE 1

Reactions of Isobutene on Calcined NH_4 Mordenites; Structure of the Products Obtained at 120°C on Aged Catalysts.

	Activation temperature T_a (°C)								
	120(MNH$_4$)	350	400	450	500	550	650	720	780
n-C_4	2	1.6	1.3	1	0.8	0.4	0.5	1	1.3
i-C_5	5.3	10.3	18.7	16.1	12.9	7.9	7.9	8.3	7.4
C_6	15.7[a]	19.1	21.3	18.2[a]	15.8	12.5	10.6	12.8	12
C_7	3.1	4.8	7.1	7.4	6.4	4	3.9	4.2	3.4
2,2,4-TMP	34.9	22.5	15.2	17.5	20	33.6	26.7	27.9	33.3
2,2-DMH	0.8	0.9	0.8	1	0.7	0.6	1	0.9	0.8
2,4-DMH + 2,5-DMH	8.4[b]	10.6	11.1	12.3[b]	13.4	10.2	13.4	12	10.8
2,3,4-TMP	29.5	28.1	21.8	23.8	27.2	29.2	32.7	30.2	29.3
2,3-DMH + 3,4-DMH	0.8	1.5	2.4	2.1	2.4	1.3	2.6	1.9	1.6
Total conversion (α%)	12.7	18.2	25.3	28.5	25	17.6	18.7	15.6	13.4
Hydrocarbon residues (mg/g)	23	25	42	58	54	24	21.1	22	25
TMP	8.2	9.2	9.4	11.8	11.7	11	11	9.1	8.4
C_5–C_7	3.2	6.5	12.3	12.3	9	4.4	4.4	4.2	3.2
DMH	1.3	2.4	3.6	4.4	4.1	2.1	2.9	2.2	1.8

[a] 2,3-DMB 80%, 2-MP 12%, 3-MP 8%.
[b] 2,5-DMH 55%, 2,4-DMH 45%.

enes and hydrocarbon residues (Fig. 1). Second, the amounts of C_5–C_7 hydrocarbons and DMH obtained on the catalysts activated at the higher temperatures (MNH$_4$(500)–MNH$_4$(720)) were larger by a factor of 1.5 than the amounts obtained on MNH$_4$, while the amounts of hydrocarbon residues were the same on nonactivated and highly activated catalysts.

Reactions of 2-Methylpropene-2-^{13}C

The discussion will be based on the observed variations with activation temperature of the product distributions of isobutene at 120°C. Before using these product distributions as chemical probes to estimate the contributions of the various active sites, it was necessary to verify that the same reaction mechanism was involved in the formation of a particular reaction product throughout the whole range of catalysts. For this reason, the reactions of 2-methylpropene-2-^{13}C were investigated on MNH$_4$ and MNH$_4$(450) and the results compared

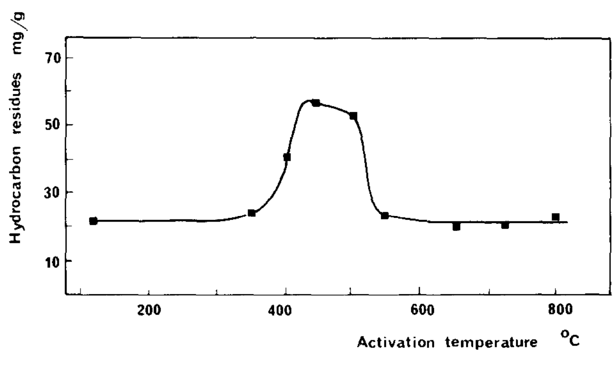


FIG. 1. Amounts of hydrocarbon residues as a function of activation temperature.

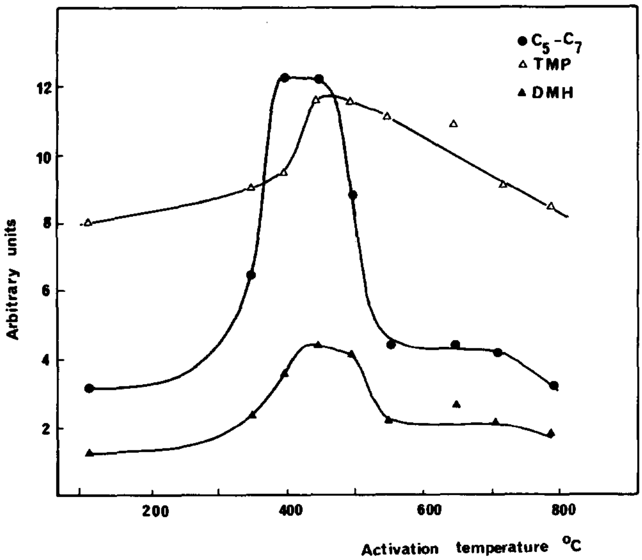


FIG. 2. Amounts of various reaction products as a function of activation temperature.

with those previously obtained on an H-mordenite activated at 550°C.

On the latter catalyst, 2,3-dimethylbutene and 2,4-dimethylpentene were partly scrambled. Four carbon atoms retained the structure and labeling of the original isobutene, while the two or three additional carbon atoms could be considered to have come from a completely scrambled C_4 unit (mechanism D). In Table 2 are reported the ^{13}C distributions of the parent ions and demethylated fragments of the 2,3-dimethylbutenes and 2,4-dimethylpentenes obtained on MNH_4 and $MNH_4(450)$. These distributions were very close to a Type D distribution, as shown by the very low mean square derivations, Δ. Similarly, as for the products obtained on H-mordenite, trimethylpentenes and 2,5-dimethylhexenes were doubly labeled in the 2–4 and 2–5 positions, respectively (mechanisms A and B, Table 3, and Fig. 4). 2,4-Dimethylhexenes retained two labels, one located on carbon 2, and the other equally distributed on carbons 4, 5, 6, and 8 (mechanism C in Table 2).

Lastly, the carbon-13 distributions of isopentenes were a combination of a Type D distribution (partial scrambling) and a Type D′ distribution, in which all five carbon atoms are equivalent and retain one-fourth of the label (Table 3). Table 3 summarizes for various reaction products and for different ions the agreement between the observed product distributions and those calculated according to mechanisms A, B, C, and D. The mean square deviations, Δ, were fairly low in all the experiments made on MNH_4, $MNH_4(450)$, and H–zeolon.

Infrared Spectra

In the ir spectra of the calcined catalysts, the intensity of the 1445-cm^{-1} band, associated with the N–H stretching frequency, decreased progressively with increasing calcination temperature. Complete disappearance of this band and therefore complete deammoniation was noted only with the catalysts activated at 500°C or higher (Fig. 5).

NaOH and NaCl Titrations

Selective titration of the protons and titration of all the cations present in the zeolite, including the cationic aluminum fragments resulting from a possible

TABLE 2

Reactions of Methylpropene-2-^{13}C on MNH_4 and $MNH_4(450)$ at 120°C; Distributions of 2,3-Dimethylbutene and 2,4-Dimethylpentene

Hydrocarbons:		2,3-Dimethylbutene			2,4-Dimethylpentene		
Distributions:		Mechanism D	Observed MNH_4	Observed $MNH_4(450)$	Mechanism D	Observed MNH_4	Observed $MNH_4(450)$
Parent ions	$^{13}C_3$	—	—	1.3	—	—	1.4
	$^{13}C_2$	39.4	40.8	39.2	59.1	60.4	58.7
	$^{13}C_1$	54.3	54.7	51.9	37.1	33.7	36.4
	$^{13}C_0$	6.2	4.5	7.5	3.7	5.8	3.5
	MSD = Δ		5	9.2		17.7	2.6
Demethylated fragments	$^{13}C_3$	—	—	0.5	—		2.1
	$^{13}C_2$	29	31.8	31.5	49.3		49.6
	$^{13}C_1$	62.2	61.2	59.6	45.7		42.3
	$^{13}C_0$	8.8	7	8.5	5		6
	MSD = Δ		12	13.3			17
Depropylated fragments	$^{13}C_2$				—	—	—
	$^{13}C_1$				77.6	78.6	77
	$^{13}C_0$				22.3	21.4	23
	MSD = Δ					1.8	1

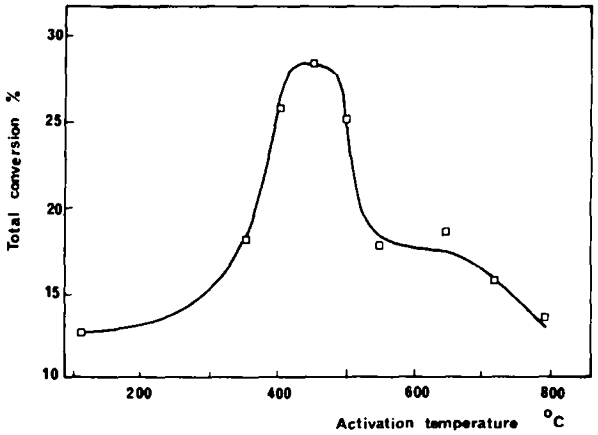


FIG. 3. Total conversion as a function of activation temperature.

dealumination (*3–5*) were carried out according to the method of Barrer and Klinowski (*4*), with NaCl and NaOH, respectively. In Table 4 are reported for various activated mordenites, from $MNH_4(450)$ to $MNH_4(780)$, the ratios between the number of exchanged sodium ions and the number of aluminum atoms present before activation, obtained according to the two methods of titration. The fact that higher values of Na/Al were obtained with the NaOH exchange method shows that none of the catalysts investigated, even $MNH_4(450)$, was pure H-mordenite and that dealumination occurred to a great extent in all of them. The number of protons, as determinated by the NaCl exchange method, decreased steadily with increasing activation temperatures beyond 500°C.

DISCUSSION

Very often maxima have been found when plotting activity versus activation temperature (*6–8*). Such maxima are generally interpreted as a result of an increase in the number or the strength of the Brønsted acid sites. Catalyzed reactions of isobutene, which allow two types of initiation steps (protonation and hydride abstraction, respectively) to be distinguished are expected to give more complete information, especially concerning the participation of weak and strong acid sites. The results presented here and summarized in Figs. 1–3 do indeed show two differrent behaviours of the mordenites with increasing activation temperature, depending on the reaction considered. The production of dimethylhexenes and of C_5–C_7 hydrocarbons was dramatically enhanced within a narrow range of activation temperatures (350–500°C), while the amounts of trimethylpentenes were only moderately affected by the pretreatment conditions.

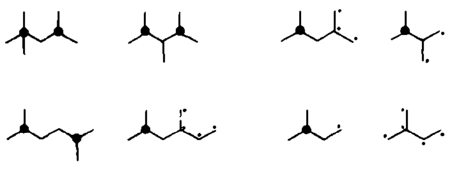
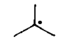
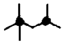
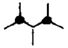
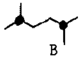
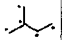


FIG. 4. Labeling of the reaction products. : labeled carbon atom; : carbon atom originating from a scrambled C_4 unit (retains one-fourth of a label).

In principle, cationic dimerization yielding TMP does not require strong acidity and should occur on any Brønsted site, of whatever strength. Indeed, the *relative* decrease of TMP from $MNH_4(450)$ to $MNH_4(780)$, shown in Fig. 6, closely parallels the *relative* decrease in the number of protons as determined by NaCl exchange. This parallelism, however, does not hold for the *absolute* decreases in activity and in the number of protons. Moreover, the increase

TABLE 3

Reactions of Methylpropene-2-^{13}C on MNH$_4$ and MNH$_4$(450) at 120°C; Reaction Mechanisms

	Hydrocarbons	Trimethylpentenes		2,5-Dimethyl-hexene	2,4-Dimethyl-hexene	2,4-Dimethyl-pentene	2,3-Dimethyl-butene	Isopentene	
	Labeling								
	Mechanisms [2]	A		B	C	D	D	D	D'
MNH$_4$ Δ	%[1]	34.9	29.5	4.6	3.8	1.8	12.5	5.3	
	Mechanism	A		B	C	D	D	0.7 D + 0.3 D'	
	Parent ions	-	12	-	-	17.7	5	1.3	
	Demet frag.	1.9	-	4.5	-	-	12	1	
	Deet. frag.	-	-	-	4.5	-	-	23	
	Deprop. frag.	-	-	-	-	1.8	-	-	
MNH$_4$(450) Δ	%[1]	17.5	23.8	6.7	5.5	4	14.5	16.1	
	Mechanism	A		B	C	D	D	0.3 D + 0.7 D'	
	Parent ions	-	9	-	-	2.6	9.2	8	
	Demet frag.	7.2	-	12.4	-	17	13.3	8	
	Deet.frag.	-	-	-	6.8	-	-	7	
	Deprop. frag.	-	-	-	-	1	-	-	
H-ZEOLON[2] Δ	%[1]	31	34.5	6.3	5	1.2	7.2	9.6	
	Mechanism	A		B	C	D	D	0.3 D + 0.7 D'	
	Parent ions	-	1.2	-	-	11	5.6	8	
	Demet frag.	0.5	-	6.5	-	-	23.4	17	
	Deet.frag.	-	-	-	5.7	-	-	7	
	Deprop.frag.	-	-	-	-	41	-	-	

[1] Percentages in the gaseous reaction products.

[2] Ref. (*1*).

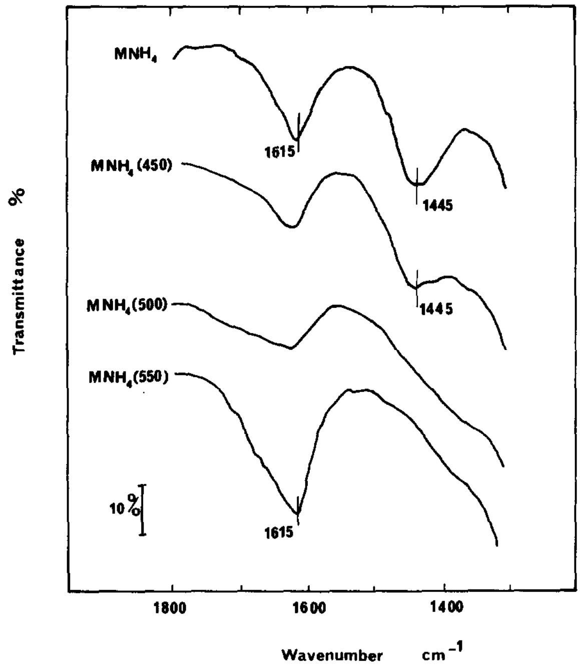


FIG. 5. Infrared spectra of activated mordenites.

of TMP with increasing activation temperatures up to 450–500°C might well be explained by the deammoniation of the zeolite, which is completed only at these temperatures. However, the substantial activity of the nonactivated NH_4 mordenite for dimerization, only 1.5 times smaller than the maximum activity, does not correspond to the actual proton content of this catalyst (one-tenth of a completely deammoniated mordenite according to analysis). From this, we conclude that the Brønsted sites are not uniform, being associated with turnover numbers differing by more than one order of magnitude. This heterogeneity, we believe, is due not to a difference in acid strength, since the ammonium mordenite is certainly less acidic than the activated catalysts, but rather to a difference in accessibility. The variations of dimerization activity in the whole range of catalysts is easily explicable by the assumption that the sites preexistent in the NH_4 mordenite, lying predominantly on the external surface, are more accessible than those created in the channels by deammoniation.

A distinct type of activity was related to the formation of C_5–C_7 hydrocarbons and dimethylhexenes. The sharp increase and decrease in the amounts of these products with increasing activation temperatures were obviously related to the sharp increase and decrease in the amounts of hydrocarbon residues formed. This observation offers a good support for the pro-

TABLE 4

Na/Al Ratios in Calcined NH_4 Mordenites Obtained by NaCl and NaOH Exchange

Activation temperature (°C)	Na/Al	
	NaOH	NaCl
450	0.90	0.46
500	0.90	0.45
550	0.92	0.37
650	0.90	0.30
720	0.71	0.19
780	0.56	0.07

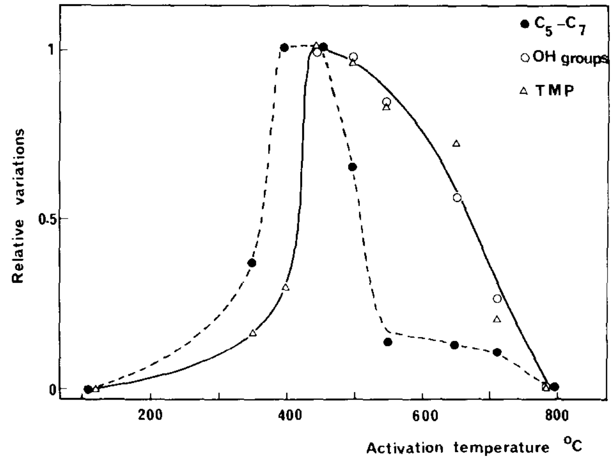


FIG. 6. Comparison between proton titration and product distributions (relative decrease of the amounts of protons and of the amounts of trimethylpentenes from $MNH_4(450)$ to $MNH_4(780)$ see text).

posal made previously (*1a*) that some of the gaseous products are, like hydrocarbon residues, obtained from hydrocarbon chains attached to the zeolite framework. Since the first step in the formation of these products is hydride abstraction, a strong acidity is required; this is better achieved by the conjunction of contiguous Lewis and Brønsted sites. Lewis sites are expected to be formed only when water is removed from the zeolite framework, and it is interesting to note that this removal, according to Weeks *et al.* (*2*), occurs at a temperature not very far from the ones at which we found an enhancement of DMH and C_5–C_7 hydrocarbons.

It was suggested previously that the production of C_5–C_7 hydrocarbons requires shorter chains, four to eight carbons long, and less acidic, more accessible sites than does that of hydrocarbon residues. In a comparison of the activity profiles for C_5–C_7 hydrocarbons with those of hydrocarbon residues and dimethylhexenes (Figs. 1 and 2), a slight shift of about 50°C towards lower activation temperatures is observed; this shift could reflect such a difference in location and acidity strength of the sites.

The sharp disappearance, at around 500–550°C, of DMH, hydrocarbon residues, and C_5–C_7 products was not related to any sharp disappearance of the Brønsted acidity and could be due to a distortion of the zeolite framework which would forbid the attachment of chains to the surface, if our hypothesis on the hydrocarbon chain precursors is correct. It has been suggested (*9*) that during the process of ultrastabilization, the zeolite passes through a number of transient states arising at much lower temperatures. It could be possible that, from one stage, attachment of hydrocarbon chains would not be possible any longer, so that all the zeolite activity associated with the formation of DMH and of C_5–C_7 hydrocarbons would be completely suppressed.

In conclusion, the catalytic reactions of isobutene at 120°C may be considered to be very sensitive chemical probes. When coupled with classical analytical techniques, such as ir spectroscopy and ion-exchange titration, these reactions not only permit weak and strong acidity to be distinguished, but also permit the relative efficiency of the various types of sites to be estimated. In this work, this chemical method of surface analysis has been used to study a series of deammoniated mordenites activated at various temperatures. The results obtained conclusively demonstrate the existence of two different types of sites associated with different reaction mechanisms.

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