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Decomposition of *n*-Butane on Alkaline-Earth Mordenites

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The acidity of alkaline-earth mordenites, as observed by the ir spectra of adsorbed pyridine, has been correlated with their activity as catalysts for *n*-butane decomposition. The results indicate that Brønsted acid sites are the origin of the catalytic activity. However, the presence of Lewis acid sites is necessary for the reaction to take place, suggesting an inductive effect of these sites on the Brønsted sites. The presence of alkaline-earth cations in decationated mordenites decreases the activity of the original sample; this influence increases with decreasing ionic radius. This result is interpreted as a weakening of the inductive effect produced by the structural Lewis sites through a fall in their number by the cation exchange process. The reactant molecules are coordinatively bound to the cations to an extent which is strongly dependent on their electrostatic field, thus influencing the accessibility of the Brønsted sites.

INTRODUCTION

As an explanation of the acidity of calcium X zeolites, Hirschler (*1*) suggested that the cation electrostatic field tends to free a proton from a hydroxyl group attached to an adjacent silicon or aluminum atom or from a water molecule adsorbed on the cation itself. Since then, several studies have been made on the interaction between the possible catalytically active sites.

Richardson (*2*) considered the possibility that the ionic potential of the cation results in a shift of the electron charge distribution toward the vicinity of the cation via a conduction band model; such an interaction would weaken the O–H bonds on the surface of the supercages and thus would modify the acidity of the hydroxyl groups. Ward (*3*) found that the concentration of Brønsted acid sites in multivalent cation zeolites appeared to be directly related to the polarizing properties of the cation. Hopkins, discussing the activity of NH_4-exchanged Y zeolite (*4*), suggested that for cracking of *n*-hexane, *n*-heptane, and ethylbenzene only the strongest Brønsted sites are catalytically effective, but the presence of Lewis acid sites is either necessary or has a synergistic effect on the activity.

Most of these experiments have been made with X or Y zeolites; however, very little information is available on mordenites, though their higher thermal stability and stronger acid sites suggest these materials as good samples for that kind of work. In a previous study on the acid sites, by ir spectroscopy using the pyridine adsorption method, Ramos (*5*) has found that, for sodium (M–Na) and decationated (M–H) mordenites exchanged with alkaline-earth cations, there are variations of the pyridinium ion band with the degassing temperature.

Some differences have also been observed in the characteristics of the Brønsted acid sites in the series M–H–Me (Me = Ba, Ca,

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Mg); when the cation field is smaller, the stability of pyridine at the Brønsted acid sites increases.

One of the most sensitive tests for detecting the possible differences in acid strength of the Brønsted sites is the use of a catalytic process. To check the previous results, the decomposition of *n*-butane has been studied using sodium and decationated mordenites as catalysts. Some additional ir spectra have also been obtained trying to correlate the Brønsted acid sites with the active sites for the above-mentioned catalytic reaction.

EXPERIMENTAL

Materials

The sodium and decationated mordenite were supplied by Norton Co. (Zeolon-100). The different samples were prepared by ion exchange with water solutions of magnesium, calcium, and barium acetates at concentrations ranging from 0.04 to 2.4 *N*. The mordenites were then filtered, washed with distilled water, and dried at 120°C for 15 hr.

The infrared cell has been described previously (*6*). The samples were prepared as self-supporting wafers under a pressure of 10 ton/cm^2 and a thickness of 10 mg/cm^2. The ir spectra were measured with a Perkin–Elmer 577 spectrometer, using an optical attenuator in the reference beam.

Method

Infrared spectroscopy. The samples were pretreated by heating under vacuum at 400, 500, 600, and 700°C for 2 hr. Pyridine was introduced under its own vapor pressure at room temperature and allowed to remain in contact with the sample for 10 min. The sample was then heated at 300°C, and after degassing for 2 hr, the transmission spectra were recorded. After successive steps of 2-hr heatings, the spectra corresponding to 400 and 500°C treatment were obtained.

n-Butane decomposition. The heterogeneous *n*-butane decomposition studies have been carried out in a fixed-bed tubular flow reactor, with He being used as a carrier gas. Reaction products were analyzed by glc (Perkin–Elmer 990), using stainless-steel columns of 2.6-m length and 0.65-cm o.d. half packed with silica gel and the remainder with Poropak Q, 80–100 mesh. Samples were taken between 30 and 100 min of reaction time; in this period of time the system can be considered to be under steady-state conditions.

Usually 0.25 g of catalyst were used. The flow rate was generally close to 100 ml/min, measured at 25°C and 1 atm; this value was chosen after observing that the external diffusion does not control the reaction above 75 ml/min.

RESULTS

(*a*) *Influence of the Thermal Pretreatment on the ir Spectra*

The study of the pyridine adsorption by ir spectroscopy to characterize the acid sites (*7, 8*) has been made on the M–H, M–H–Ca (21%), and M–H–Mg (40%) mordenites pretreated at 400, 500, 600, and 700°C. In Fig. 1a, the area values of the band at 1548 cm^{-1}, corresponding to the Brønsted acid sites, are plotted against the pretreatment temperature, T_P. These numbers are the mean values of at least three spectra obtained with three different samples. The degassing temperatures, T_D, were 400 and 500°C. It has been considered that, if there were several types of Brønsted acid sites, the band area would yield more information than the band height. In all cases, the values of the band decreased strongly when the samples were pretreated above 500°C. In Fig. 1b, the values for the samples M–H and M–H–Mg pretreated at 500°C and degassed at 300, 400, and 500°C are presented. A faster decrease of the area was observed with the M–H–Mg sample. The values of the M–H–Ca sample are in the middle. This variation with T_D indicates

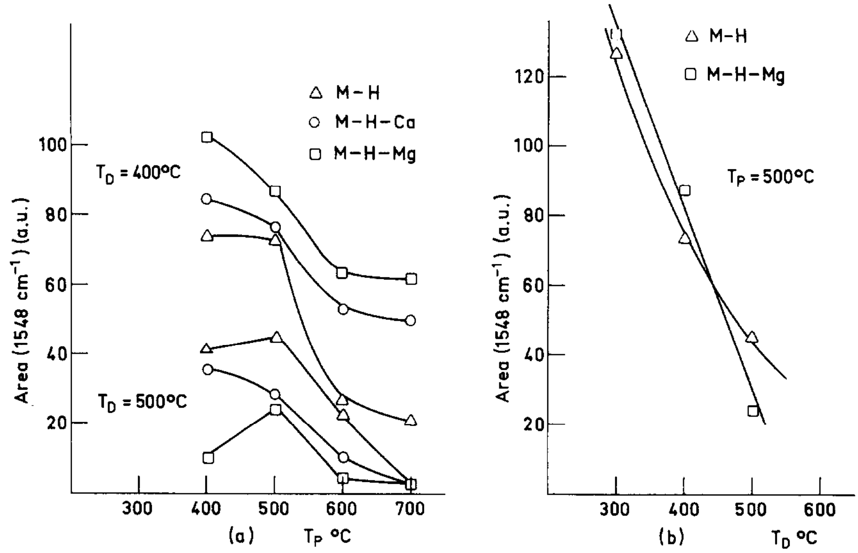

FIG. 1. (a) Area variation of the band at 1548 cm^{-1} with pretreatment temperature (T_P). Degassing temperature (T_D): 400 and 500°C. (b) Area variation of the band at 1548 cm^{-1} with degassing temperature (T_D). Pretreatment temperature (T_P): 500°C.

that the Brønsted acid sites have different characteristics, fixing the pyridinium ion in a way which is less stable in the order M–H–Mg < M–H–Ca < M–H.

There are at least two bands due to pyridine coordinatively bound to alkaline earth metal atoms or tricoordinated aluminum atoms. It appears that the pretreatment temperature does not influence, in an appreciable way, the amount of coordinated pyridine. However, the variation of the band height with T_D is different for the three samples. In the case of M–H–Ca, the band at 1449 cm^{-1} decreases, and at 400°C, it is only a shoulder in the Lewis acid band. The variation for the samples M–H–Mg (pyridine coordinatively bound to Mg^{2+}) and M–H (proper Lewis acid sites) is different; the former remains almost constant, and the latter increases in the temperature range studied.

Though the exchange cations are also Lewis acids, we shall consider the tricoordinate aluminum lattice ions as the proper Lewis acids. This difference appears in almost all papers dealing with catalysis on zeolites and is justified by the results.

For most samples, two bands have been observed for the proper Lewis acid sites, at 1455 and 1464 cm^{-1}. These bands were assigned by Cannings (*9*) to two sites with different acid strengths. No significant change of the relative height of the two bands has been observed with increasing pretreatment temperature. When the pyridine was degassed at 700°C, both bands disappeared; at lower temperature the band at 1464 cm^{-1} was a shoulder on the highest band at 1455 cm^{-1}.

(*b*) *Influence of the Thermal Pretreatment on the Transformation Rate of n-Butane*

Experiments were carried out using a M–H–Ca (21%) catalyst pretreated at different temperatures in helium for 15 hr. Other conditions were: catalyst weight, 0.25 g; *n*-butane partial pressure, 0.25 atm; total feed flow, 76 ml/min, N.C., and reaction temperatures, 400 and 500°C. The values shown in Table 1 (product distribution) and in Fig. 2 (cracking + isomerization conversion) correspond to samples obtained after 60 min of operation. A gradual

TABLE 1

Catalyst: M–H–Ca (21.3%)

Catalyst pretreatment temperature (°C)	Product distribution (mol%)						
	CH_4	C_2H_6	C_2H_4	C_2H_8	C_3H_6	C_4H_8	i-C_4H_{10}
	Reaction temperature: 400°C)						
680	4.04	10.41	2.98	22.42	6.27	16.26	37.62
600	3.86	5.21	3.64	27.03	3.05	5.67	51.54
500	3.64	6.47	3.50	31.10	2.65	3.83	48.81
420	3.95	5.20	3.55	28.98	2.71	4.13	51.84
	Reaction temperature: 500°C						
680	19.45	12.60	8.90	17.83	10.62	15.32	15.28
600	12.64	7.17	8.98	33.95	7.87	6.94	22.45
520	13.11	7.36	9.78	35.07	8.28	7.08	19.32

decrease of activity is observed above a pretreatment temperature of 500°C.

(c) *Influence of the Exchanged Cation on the Decomposition Rate*

This study was made with sodium and decationated mordenites exchanged with magnesium, calcium, and barium cations, at different concentrations.

In Fig. 3, the results obtained for n-butane decomposition, using commercial M–H, pure and exchanged with the different cations, are plotted vs the cation concentration. Data were obtained at the following experimental conditions: catalyst pretreatment temperature, 680°C, 15 hr (helium); reaction temperature, 600°C; catalyst weight, 0.25 g; n-butane partial

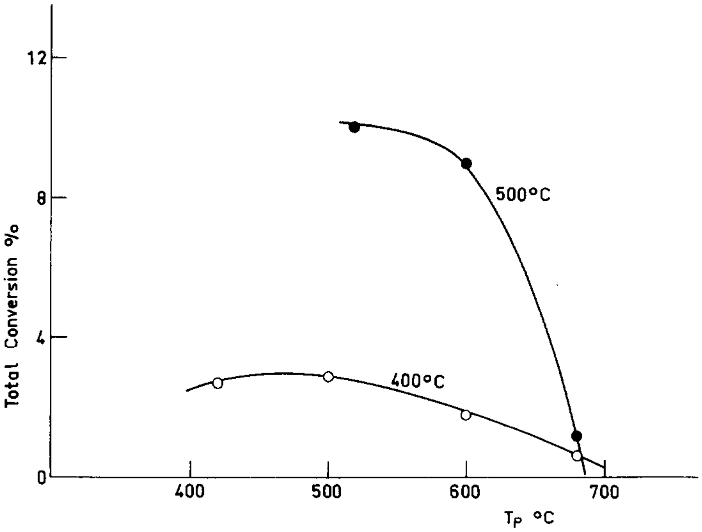

FIG. 2. n-Butane total conversion vs pretreatment temperature (T_P) for M–H–Ca (21%). Reaction temperatures: 400 (●) and 500°C (○).

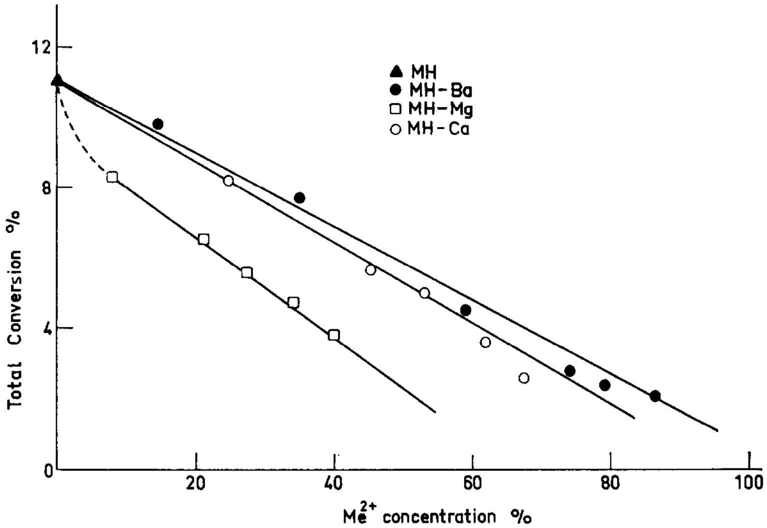

FIG. 3. n-Butane total conversion vs alkaline-earth cation concentration.

pressure, 0.27 atm; total feed flow, 103.8 ml/min, measured at 25°C and 1 atm.

Samples were taken between 30 and 100 min of operation time. During this time the activity and selectivity of the studied catalysts remained constant.

Figure 3 shows that sample M–H is the most catalytically active in this process. When some alkaline-earth cations are introduced, a fall in butane total conversion is observed, increasing with cation concentration. However, this loss is not independent of the cation: At the same degree of exchange the catalytic activity follows the sequence M–H–Ba > M–H–Ca > M–H–Mg. This is the same order as the values of ionic radius, or inverse order of electronegativity.

The product distribution obtained for different M–H-exchanged mordenites is presented in Table 2. Operating conditions were the same as before, though the catalyst weight was changed in order to obtain similar conversion values.

In the above experimental conditions, cation-exchanged sodium mordenites did not show any activity.

DISCUSSION

The results shown in Table 2 indicate that there is no effect of the cation exchanged on the product distribution. This suggests that the nature of the active centers of the decationated mordenite does not change sensitively with the presence of the alkaline-earth metals.

TABLE 2

Reaction Temperature: 600°C

Catalyst	x_T (mol%)	Product distribution (mol%)						
		CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_8	i-C_4H_{10}
M-H	7.6	25.3	11.8	10.9	6.1	23.5	17.3	5.1
M-H-Ca (21.3%)	7.3	23.8	12.5	12.1	5.9	23.2	20.0	2.5
M-H-Mg (21.1%)	6.5	25.2	11.7	11.1	4.9	22.7	19.4	4.9
M-H-Ba (45.2%)	8.0	25.6	12.3	11.9	6.0	24.3	19.3	0.5

The thermal pretreatment of the samples has an important influence on the catalytic activity, as observed in Fig. 2. It shows a fall of activity for pretreatment temperature above 500°C. The ir band related with coordinatively bound pyridine is very slightly affected by T_P, but the band corresponding to pyridinium ions presents a similar drop at the same temperature. Thus, the catalytically active sites should be related with the Brønsted acid sites.

The strong presence of Lewis acid sites at temperatures lower than that of dehydroxylation (~450°C) has already been observed by Becker *et al.* (*10*) and represents a different behavior of the commercial M–H compared to other zeolites.

The cation exchange can also produce Brønsted sites according to the mechanism (*12*):

$$Me^{2+} + (H_2O) \rightleftharpoons Me^{+}(OH) + H^{+} \quad (1)$$

However, not all Brønsted acid sites measured at low T_D can be responsible for the catalytic activity. In samples M–Na–Me, in which sodium mordenite is used for cation exchange, though a band corresponding to Brønsted acid sites has been observed (*11*), no catalytic conversion has been detected.

The Brønsted acid sites in M–H, the most active catalyst for the present reaction, keep pyridinium ions bound at a higher temperature (T_D = 500°C) than those in all the other samples. When alkaline-earth cations are introduced, there is a decrease in catalytic activity, and the Brønsted acid sites band decreases faster with increasing degassing temperature.

All these results seem to indicate that only a certain type of Brønsted acid site present in the decationated mordenites is catalytically active.

A strong loss of activity has also been observed by Becker *et al.* (*10*), for alkylation of benzene, when magnesium cations are exchanged into M–H.

When alkaline-earth cations are introduced into the M–H sample, some original Brønsted sites are lost, but new ones are created by mechanism (1). The infrared spectra, at low degassing temperature, show an increase of the band at 1548 cm^{-1} and a fall in the Lewis acids band, which suggest that the number of tricoordinated aluminum ions is also affected by the cation exchange. If the effect of the exchanged cations were simply to induce the formation of Brønsted sites and to reduce the number of Lewis sites, the loss of activity would be the same for all the cations, but the results shown in Fig. 3 indicate that this is not the case.

Hair (*13*) has suggested that Lewis acid sites have an inductive effect on the nearby Brønsted sites, increasing their acid strength. The alkaline-earth cations, decreasing the number of Lewis centers, will affect the behavior of some pyridinium ions. However, they must have a further influence which should depend on their electrostatic field.

Although the cations are also Lewis acid sites, the difference with the tricoordinated aluminum is in the fact that the latter are in the lattice, strengthening the Brønsted sites, but the former are "extra-framework," in the channels of the mordenite, in competition with the Brønsted sites to bind the pyridine or butane molecules. At high temperatures the cations keep the pyridine bound more strongly than the Brønsted sites (*11*); in this way they reduce the number of molecules available to these sites. This effect will depend on the electrostatic field of the cation, being stronger, in the present case, for Mg^{2+}, which shows the lowest activity.

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