

# REACTION OF ETHYLENE OVER HYDROGEN MORDENITE, BERYLLIUM MORDENITE, AND LANTHANUM MORDENITE

By

H. G. KARGE and J. LADEBECK  
Berlin-West

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The conversion of ethylene over the catalysts hydrogen mordenite, beryllium mordenite, and lanthanum mordenite has been studied using a flow reactor. The reaction yielded light hydrocarbons and polymerisate (coke) as detected by G. C., M. S. and IR. Acid OH groups proved to be the active centers. The IR results suggest rapid formation of carbonium ions in the case of the most acid, highly active hydrogen mordenite, whereas over the less acid beryllium mordenite and lanthanum mordenite initially  $\pi$ -complexes have formed, transforming only slowly to carbonium ions. These results offer an explanation of the differences in activity and life-time of the catalysts.

## Introduction

In some previous papers [1—3], we have thoroughly studied the catalysis of benzene alkylation by olefins as well as the inverse reaction (dealkylation). Commercial hydrogen mordenite (HM), the catalyst which was first applied by us for these reactions, exhibited high activity and significant selectivity, due to its special pore geometry (shape selectivity) [1]. Preferentially monoalkylbenzene and, to a smaller extent, only *p*- and *m*-dialkylbenzenes had formed. Unfortunately, the HM was rapidly deactivated. This was attributed to olefin polymerisation (also catalyzed by HM) and subsequent coking. Beryllium mordenite (BeM) and lanthanum mordenite (LaM), prepared by ion exchange from Na-mordenite and being even more selective, exhibited a much prolonged life-time [2—3]. IR evidence suggested that in every case acid OH groups of the zeolite catalysts were the active sites. However, preliminary experiments showed significant differences in the strength of interaction between ethylene and the OH groups of the respective catalysts HM, BeM, and LaM. It was the aim of the present work to study this different behavior of HM, BeM, and LaM in more detail.

## Experimental

The IR spectra were run with a spectrometer model 325 (Perkin—Elmer). Our IR cell was a modification of the cell designed by KNÖZINGER ET AL. [4]. The commercial HM was supplied by the Norton Company, Mass. BeM and LaM were exchanged to 59% and 64%, respectively. For technical and experimental details of the IR and catalytic studies see [3] and [5]. Prior to the reaction, the zeolites had

been calcined at the activation temperature  $T_A$  (usually 723 K) under dynamic vacuum (usually  $1.33 \times 10^{-2}$  Pa  $\cong 10^{-4}$  torr). The reaction temperature  $T_R$  was usually 723 K as well. Ethylene/helium mixtures were applied, the partial pressure of ethylene being  $3.33 \times 10^3$  Pa ( $\cong 25$  torr).

### Results

#### Reaction of Ethylene over HM, BeM, and LaM

Figs. 1a and 1b show the total conversion  $\varphi_{\text{tot}}$  of ethylene and the conversion  $\varphi_{\text{hc}}$  to light hydrocarbons varying with time  $t_R$ . The difference  $\varphi_{\text{tot}} - \varphi_{\text{hc}}$  gives the conversion  $\varphi_{\text{poly}}$  to polymerisate and/or (at higher temperatures) to coke. The most striking feature in Fig. 1a is the instantaneous onset of the reaction in the case of

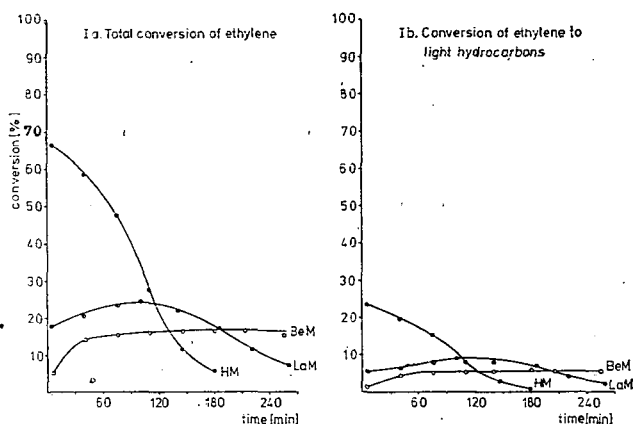


Fig. 1. Conversion of ethylene over HM, LaM, and BeM.  $T_A = T_R = 723$  K; pressures:  $p_E = 3.33 \cdot 10^3$  Pa and  $p_{He} = 1.00 \cdot 10^5$  Pa;  $u = 30$  ml/min. ethylene/helium gas mixture; mass of catalyst: 0.25 g

HM, followed by a rapid decrease of the conversion, whereas BeM exhibits a pronounced incubation period with increasing  $\varphi$ , reaching then a steady state for several hours. With the exception of the incubation period, this  $\varphi/t_R$  dependency corresponds to that observed during the alkylation process [3]. LaM is intermediate between HM and BeM. The situation is quite similar in Fig. 1b (formation of light hydrocarbons). Table I presents the product distributions after  $t_R = 40$  min. Over HM, propane had preferentially formed, whereas over BeM propene was mainly produced. The ratio  $s = \text{saturated hydrocarbons} / \text{unsaturated hydrocarbons}$  decreases with the sequence HM, LaM, BeM. The composition of the hydrocarbon mixture varies over BeM only slightly with time ( $t_R > 40$  min.). Over HM,  $s$  decreases from 3.44 at the beginning of the reaction to 1.44 at  $t_R = 2$  h. The same behavior of the conversion  $\varphi_{\text{hc}}$  and the product distribution had been observed during the alkylation; *i.e.*, in the presence of benzene, ethylbenzene, etc. With dehydroxylated HM and BeM ( $T_A = 973$  K;  $T_R = 723$  K), the starting conversions  $\varphi_{\text{tot}}$ ,  $\varphi_{\text{hc}}$ ,  $\varphi_{\text{poly}}$  amounted to only 10% of those

Table I  
Conversion and Product Distribution in Percent

	Catalyst	$\varphi_{\text{tot}}$	$\varphi_{\text{po1}}$	$\varphi_{\text{hc}}$	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	s
$T_A=723$ K	HM	58.7	39.0	19.7	1.6	2.6	1.9	9.8	2.9	0.9	3.1
	LaM	20.8	14.2	6.6	0.5	0.7	3.8	0.8	0.5	0.3	0.5
$T_R=723$ K	LaM	14.2	10.0	4.2	0.3	0.5	2.8	0.2	0.2	0.2	0.4
	BeM										
$T_A=923$ K	HM	5.4	3.7	1.7	0.1	0.1	1.3	—	0.1	0.1	
	LaM	2.4	2.3	0.1	0.05	—	0.07	—	—	—	
$T_R=723$ K	BeM	1.6	1.4	0.2	0.1	—	0.1	—	—	—	

found over the hydroxylated forms (Table I). In the case of HM the activity decreased further with increasing  $t_R$ . In contrast, over BeM the conversion slowly increased with time after three hours had reached the four-fold of the starting value. — Both HM and BeM showed a distinct maximum of  $\varphi_{\text{tot}}$  and  $\varphi_{\text{hc}}$  at  $T_R=673$  K. (Above 673 K dehydroxylation became noticeable, as could be seen by IR.)

### IR spectroscopic investigations

Fig. 2 compares the spectra of (hydroxylated) HM and BeM before and after adsorption of ethylene at  $1.33 \times 10^4$  Pa ( $\cong 100$  torr) and the temperature attained by the sample in the IR beam (B. T.  $\approx 373$  K). In the case of HM (Figs. 2a, 2b, spectrum 2), the bands of exclusively saturated hydrocarbons appear immediately ( $\nu_{\text{as}}^{\text{CH}_3}$ : 2950

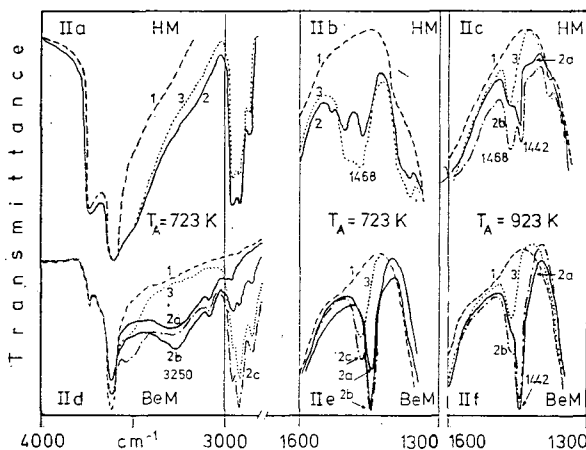


Fig. 2. IR spectra of HM and BeM before (spectra 1) and after (spectra 2) interaction with ethylene at B. T. Ethylene pressure  $p_E = 1.33 \cdot 10^4$  Pa, excepted Figs. 2 a, b, d, e — spectra 2 and 2a, where  $p_E = 3.33 \cdot 10^3$  Pa. Time of interaction  $t_R \approx 15$  min., excepted Figs. 2 d, e — spectra 2c, and 2 c, f — spectra 2b, where  $t_R = 15$  h. After pumping: spectra 3. Further details see text.

$\text{cm}^{-1}$ ;  $\nu_{as}^{\text{CH}_2}$ :  $2930 \text{ cm}^{-1}$ ;  $\nu_s^{\text{CH}_2}$ :  $2860 \text{ cm}^{-1}$  and a broad  $\delta_{as}^{\text{CH}_2}$  band at  $1468 \text{ cm}^{-1}$ . The OH band at  $3600 \text{ cm}^{-1}$  has been weakened remarkably. These changes in the spectrum are practically irreversible at B. T. (Figs. 2a, 2b, spectra 2, 3). In the spectrum of BeM (Figs. 2d, 2e), the sorption of ethylene causes also a significant decrease (about 75%) of the OH band intensity. Simultaneously, a broad band at  $3250 \text{ cm}^{-1}$  appears, indicating the formation of a  $\pi$ -complex. Further bands (spectrum 2a in Figs. 2d, 2c) are exclusively ascribable to olefinic species ( $\nu^{\text{CH}}$ :  $3030 \text{ cm}^{-1}$ ,  $\delta^{\text{CH}_2}$ :  $1442 \text{ cm}^{-1}$ ). At higher pressures and prolonged time, respectively, also the signals of saturated hydrocarbons appear (spectrum 2c), persisting even during pumping at B. T. Comparing dehydroxylated HM and BeM ( $T_A = 973 \text{ K}$ ), Figs. 2c, 2f demonstrate the appearance of olefinic bands ( $1442 \text{ cm}^{-1}$ ) in both cases. Only after a long period of interaction (15 h) could bands of saturated species be detected; these bands remained in the spectrum after pumping. Both dehydroxylated zeolites were only slightly rehydroxylated during the experiment.

At  $573 \text{ K}$  and  $3.33 \cdot 10^3 \text{ Pa}$  (25 torr) the following changes were observed: With (hydroxylated) HM only very weak and vague CH bands were detected, the OH band being less weakened than at  $373 \text{ K}$  (Fig. 3a, spectrum 2a). Instead, a broad and intensive absorption around  $1585 \text{ cm}^{-1}$  developed (Fig. 3b, spectrum 2a) due to coke formation [6—8]. The sample became black. In the case of dehydroxylated

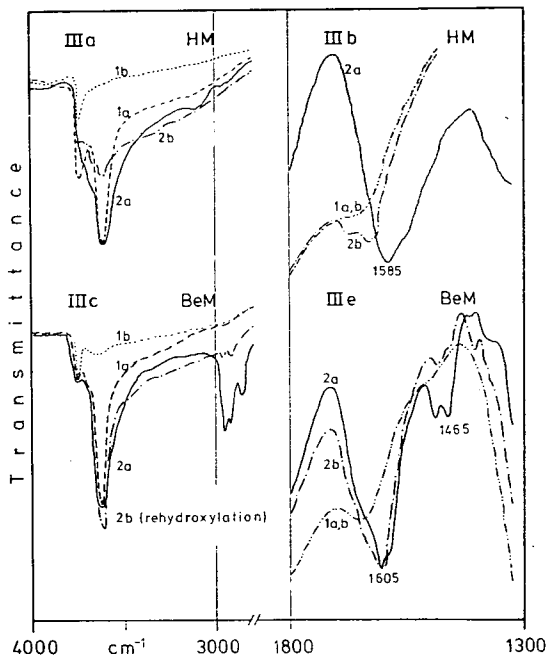


Fig. 3. IR spectra of HM and BeM before (spectra 1) and after (spectra 2) interaction (90 min.) with  $3.33 \cdot 10^3 \text{ Pa}$  ethylene at  $573 \text{ K}$  and subsequent pumping (to  $1.33 \cdot 10^{-4} \text{ Pa}$ ) at B. T. Spectra 2a: interaction with hydroxylated forms (1a); spectra 2b: interaction with dehydroxylated forms (1b). Further details see text.

HM ( $T_A=923$  K) no CH bands whatsoever appeared, even at  $1585\text{ cm}^{-1}$  (Fig. 3b, spectrum 2b). The sample remained white and was rehydroxylated to a low extent (15%) (Fig. 3a, spectrum 2b). The differences between hydroxylated and dehydroxylated BeM were less pronounced. In fact, the CH bands appearing on ethylene interaction were more intensive in the first case (Fig. 3c, compare spectra 2a and 2b). However, both forms showed polyolefin formation after a sufficiently long period of interaction (band at  $1605\text{ cm}^{-1}$ , being indicative of olefinic groups in a conjugated polyene type structure [6—7]). Similar observations were reported by WEEKS AND BOLTON [9] in their work on olefin-zeolite intermediates, using 1-butene and HY. Surprisingly, the BeM had been completely rehydroxylated during the ethylene interaction (Fig. 3c, spectrum 2b). (The ethylene applied contained traces of  $\text{H}_2\text{O}$  and  $\text{O}_2$ .) At still higher temperatures (723 K) one finds in general the same differences between HM and BeM: In the case of HM, there is more significant weakening of the OH band, more polymerizate and subsequent coke formation (band at  $1585\text{ cm}^{-1}$ ). With BeM, there is a tendency to rehydroxylation, and rather polyene formation (band at  $1605\text{ cm}^{-1}$ ) after longer exposure. Using BeM, oxidation of the deposit often occurs, indicated by a  $\text{CO}_2$  band at  $2350\text{ cm}^{-1}$ .

#### Mass spectrometric investigations

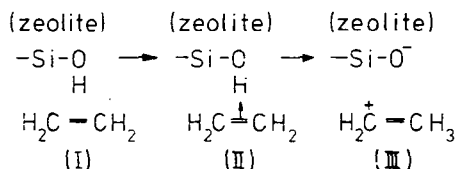
The BeM sample, the spectrum of which is shown in Figs. 3c and 3d, spectrum 2a, has been slowly ( $5^\circ/\text{min.}$ ) heated to 673 K. During the heating mass spectra were run. Above  $T_{\text{Des}} \approx 373$  K signals appeared ascribable to desorbed hydrocarbon species:  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_4\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$  and fragments of the approximate composition  $\{\text{CH}\}_n$  ( $n=1-7$ ). Table II gives the masses observed, their assignments, and the temperatures of highest signal intensity.

Table II

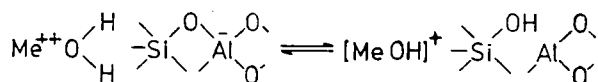
Mass	Species	Mass	Species	T
14, 15, 16	$\text{CH}_4$	12, 13, 14	$\text{CH}_2$	360
26, 27, 28	$\text{C}_2\text{H}_4$	37, 38, 39	$\{\text{CH}\}_3$	300
29	$\text{C}_2\text{H}_5^+$	50, 51, 52	$\{\text{CH}\}_4$	380
41, 43	$\text{C}_3\text{H}_6$	63, 65	$\{\text{CH}\}_5$	380
55, 56	$\text{C}_4\text{H}_8$	77, 78	$\{\text{CH}\}_6$	410
57, 58	$\text{C}_4\text{H}_{10}$	91, 92	$\{\text{CH}\}_7$	410

#### Discussion

Obviously, HM contains OH groups of higher acid strength than BeM and LaM, which is in analogy to the results on  $\text{HY}/\text{Me}^{++}\text{Y}$ . This provides an explanation of the higher starting activity of HM (Fig. 1). Thus, according to



over HM a great number of carbonium ions (structure III) will immediately form upon ethylene exposure, initiating the polymerization. In the case of BeM, the olefin is partially physisorbed, partially bound as a  $\pi$ -complex (structure II, see also Fig. 2d, spectrum 2b). The  $\pi$ -complexes only slowly transform to structure III, as could be evidenced by IR. This causes the incubation period and the lower reaction rate over BeM and LaM compared with HM (Fig. 1). In principle, the formation of polymerizate and consequently the blocking of the active centers (acid OH groups) is the reason for the catalyst deactivation at lower temperatures ( $\approx 373$  K). At higher temperatures the polymerizate is destroyed and the OH groups are partially liberated. However, the increasing amount of coke will obstruct the zeolite pores more or less rapidly. HM shows fast formation of polymerizate and coke, and therefore rapid deactivation (Figs. 1, 2a, b, 3a, b). The longer life-time of BeM is probably due to two effects: (a) the lower conversion  $\varphi_{\text{poly}}$  allows for sufficient removal of deposits during the reaction (to some extent by oxidation), and (b) with BeM OH groups may be regenerated via rehydroxylation (Fig. 3c, spectrum 2b). This compensates for the usual loss of activity due to removal of OH groups (dehydroxylation) during prolonged reaction time. The rehydroxylation of BeM can be well understood on the basis of the HIRSCHLER scheme [10]:



Dehydroxylation leads to a reformation of bare  $\text{Be}^{++}$  cations and not to irreversible changes in the lattice structure as in the case of HM [11–12]. Accordingly, no newly formed Lewis sites could be identified via pyridine adsorption after dehydroxylation of BeM and LaM. Subsequent exposure of the dehydroxylated BeM to  $\text{H}_2\text{O}$  vapor at higher temperatures restores the acid OH centers and  $\text{Be}(\text{OH})^+$ , according to the above scheme.

The mass spectra run during the desorption shows, in general, the same products as found by GC during the reaction. To a large extent, particularly on HM, the  $\{\text{CH}\}_n$  deposits form at the beginning of the reaction. Presumably they are originally richer in hydrogen and can serve as a source for hydrogenation. The role of "carbonaceous deposits" and fragments with C:H ratio close to 1 in intermolecular hydrogen transfer (yielding saturated hydrocarbons) has been studied and discussed by ÖRHALMI AND FEJES [13]. This would offer an explanation for the fact that over (hydroxylated) HM primarily saturated hydrocarbons are formed.

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