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Benzene Alkylation with Ethylene and Propylene over H-mordenite as Catalyst

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The distributions of products indicate the catalytic selectivity of H-mordenite, which must be expected on the basis of the special pore structure of this zeolite. Likewise, for steric reasons the ratio of *m*- and *p*-dialkylbenzene is reversed, when propylene is used instead of ethylene. Catalyst aging is caused by olefin polymerization. The lifetime of the catalyst is increased after diluting the olefin with helium and increasing the reaction temperature. The catalyst exhibits optimum activity at an activation temperature of 450°C. As can be concluded from a correlation with ir results, concerning the temperature dependence of Brønsted- and Lewis centers, the Brønsted—OH groups are the active sites. The relatively low apparent activation energy of 10 kcal/mole for the conversion to ethylbenzene is discussed.

In the range of 0 to 200 Torr the benzene conversion increases with benzene pressure. The benzene conversion shows a distinct maximum at about 30 Torr of ethylene pressure, while keeping the benzene pressure constant at 200 Torr.

INTRODUCTION

The catalysis by means of zeolites has been studied for a great number of very different reactions (*1–3*), including the zeolite catalyzed alkylation of benzene by olefins (*4–7*). However, in the studies concerned with the latter reaction, almost exclusively faujasite-like zeolites of the Linde X and Linde Y type have been used as catalysts. In the present work another zeolite, namely H-mordenite was chosen for the following reasons. H-mordenite is well known to be a very active catalyst for certain reactions, e.g., alkylation or *o*-xylene isomerization (*8–14*). On the other hand, this molecular sieve is characterized by a special system of parallel channels (*15*). Comparing the diameters of these channels (7.1 Å × 5.9 Å) with the dimensions of the benzene molecule (6.8 Å × 6.2 Å × 3.2 Å), one would expect a high degree of selectivity. That means the production of monoalkylbenzenes and *p*-dialkylbenzenes should be favored (*8, 11, 16*). This assumption was tested and verified by analysis of the product distribution under various conditions of the reaction.

Furthermore, two questions were of great interest. Firstly, on what active sites does the reaction take place? In the case of zeolites, it was suggested that either Brønsted–OH groups (*13, 17–24*), or Lewis acid centers (*25, 26*), or the cations of exchanged molecular sieves (*27, 28*) are the loci of catalytic activity. Secondly, how do the reaction parameters, such as temperature and pressure of the reactants determine the kinetics of the reaction? To clarify these questions the influence of the following parameters on the conversion rate has been studied: pretreatment temperature, temperature of reaction, partial pressures, and poisoning by olefinic polymerization. The results of some of these experiments could be correlated to ir spectroscopic investigations of the same system (*29*).

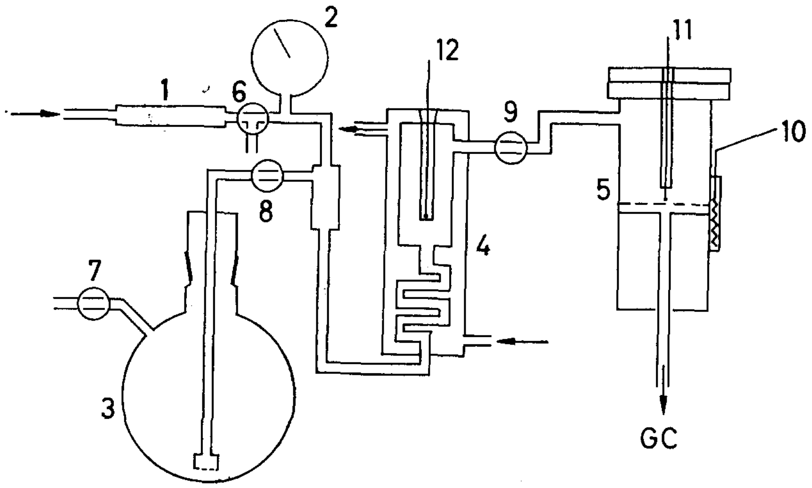

FIG. 1. Scheme of the apparatus: (1) desiccator; (2) manometer; (3) storage-vessel for benzene; (4) saturator; (5) reactor vessel; (6) three-way cock; (7–9) stop-cocks; (10) resistance thermometer; (11, 12) thermocouples; (GC) gas chromatograph.

EXPERIMENTAL SECTION

Materials

H-mordenite was supplied by the Norton Co., Mass.* with a composition (in wt %) of: 74.5 SiO_2, 9.0 Al_2O_3, 0.5 Na_2O, and 16.0 components volatile in high vacuum at 800°C, especially H_2O. The Si/Al ratio was 7:1, and the formal evaluated BET surface was 500 m^2/g, according to the data given by the manufacturers. The zeolite powder was purified by heating it at 5°/min up to 350°C and calcining it at this temperature for 30 min in flowing air, which was saturated with water vapor at room temperature, in order to prevent loss of OH groups. It has been established by X ray and ir, that this purifying procedure does not affect the crystallinity of the material. However, the behavior of H-mordenite remained unchanged after purification in a stream of dry air. Benzene (*pro analysi* and gas chromatography grade) was obtained from Riedel de Haen AG., Hannover, and was dried with Linde A5. Ethylene, propylene, and olefin/helium mixtures (1–15 volume % ethylene, 6 volume % propylene) were delivered by the Messer Griesheim GmbH.

Apparatus

A schematic drawing of the apparatus is shown in Fig. 1. The reactor vessel (5), which could be heated resistively to 650°C, was made of stainless steel and could be closed by a vacuum proof Varian flange. A stainless steel sieve for supporting the catalyst was mounted just below the thermocouple (11). The gases (ethylene, propylene, olefin/helium) were saturated with benzene vapor, by passing them through the evaporator (4) before they entered the reactor (*30*). The benzene vapor pressure was adjusted by changing the temperature of the thermostatting water flux in the saturator jacket. In order to prevent condensation of benzene or products all feed lines were heated sufficiently. The gases were analyzed by means of a Perkin–Elmer gas chromatograph, type F 6 (column: Golay 2 G, apiezon, 25 m; column temperature: 120°C; carrier gas: H_2).

Procedure

The catalyst samples (0.1–1.0 g) were placed onto the supporting sieve. In the usual case of catalyst powder the thickness

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* We thank the Norton Company for generously supplying the mordenite samples.

of the catalyst bed was about 1 mm. (There was no change in the results, when in some experiments catalyst platelets were used, which had been pressed under a pressure of 2000 kP/cm^2 and were about 0.1 mm thick.) Then the reactor, containing the appropriate charge of catalyst, was heated to the desired calcination temperature. This temperature was maintained for 0.5 hr. During this activation process and the subsequent cooling to the reaction temperature, the reactor was evacuated to 10^{-2} – 10^{-1} Torr. Finally, the evacuated reactor was filled always with a feed gas (olefin; olefin/benzene; olefin/helium/benzene) to a total pressure of one atmosphere.

A pulse of the gaseous reactant mixture was introduced in certain intervals into the gas chromatograph for analysis. In order to meet the condition of a differentially working flow reactor, the mass m of the catalyst samples was limited in such a way that the degree of conversion did not exceed ca. 10% of the input benzene. The mass balance for a flow reactor leads to the following equation:

$$\frac{V_R}{u} = -\int_{c_0}^{c_e} \frac{1}{r_R(c)}\, dc \qquad (1)$$

[V_R: volume of the catalyst bed (cm^3); u: velocity of flow (cm^3/min); $r_R(c)$: rate of reaction (mole/cm^3 min); c: concentration of the reactant in question (mole/cm^3); c_0: input concentration (mole/cm^3); c_e: output concentration (mole/cm^3)].

For the case of a differential flow reactor, the change in concentration and, therefore, the degree of conversion $\varphi = (c_0 - c_e)/c_0$ of the reactant in question must be kept small enough so that r_m can be considered as a constant. Then, a linear relationship is obtained between r_R and φ, i.e.,

$$r_m = (u/m) \cdot c_0 \cdot \varphi \qquad (2)$$

(m: mass of the catalyst sample (g); r_m: reaction rate per gram catalyst). Thus, if one changes only u and keeps all other parameters constant, a straight line in the φ $(1/u)$—plot must be obtained. These requirements were fulfilled in the range from 10 to 50 cm^3/min for the conditions of the following experiments.

RESULTS

Selectivity

In the case of alkylation by ethylene, monoethylbenzene was the main product, when the reaction temperature was below 300°C. Only small amounts of *m*- and *p*-diethylbenzene and naphthalene were formed. Above 300°C the catalyst lost its selectivity and other components, such as toluene and larger amounts of naphthalene, were among the products. H. Hopff and H. Ohlinger (*31*) have pointed out that naphthalene may be formed via *o*-diethylbenzene and *o*-divinylbenzene. The retention time of the "other" products was always shorter than that of naphthalene and symmetric trialkylbenzene, and in most cases even shorter than the retention times of dialkylbenzenes. Therefore it is unlikely that higher alkylated and bigger molecules were formed. Alkylation with propylene yielded a larger portion of dialkylbenzenes when compared at temperatures below 300°C. At higher temperatures (400°C), the amount of these components decreases but other unidentified products were formed.

It is considered from a comparison of the GC results of the test mixtures, that probably butylbenzenes and cracking products were among the "other" products. The amount of them decreased very rapidly with the reaction time as toluene and naphthalene did. However, within the limits of temperatures below 300°C the considerations of the following sections are not affected by the loss of catalyst selectivity.

Typical examples of product distributions obtained after a reaction time of 12 min at various temperatures are given in Table 1.

Polymerization and Catalyst Poisoning

The conversion φ_B of benzene decreases as a function of time in a nearly exponential manner (Fig. 2) because the catalyst sample is progressively poisoned during the reaction. To eliminate uncertainty in evaluating the experimental data, log φ_B was plotted as a function of time t and the resulting straight lines were extrapolated

TABLE 1
PRODUCT DISTRIBUTION IN WEIGHT PERCENT[a]

Ethylene/Benzene				Propylene/Benzene				
Product t_R[°C]	100	150	400	Product t_R[°C]	80	100	150	400
Ethylbenzene	93.5	77.2	60.0	Cumene	68.9	60.9	53.4	62.1
m-Diethylbenzene	3.7	8.6	2.1	*m*-Diisopropylbenzene	7.3	9.6	17.4	0.2
p-Diethylbenzene	2.8	5.4	1.9	*p*-Diisopropylbenzene	23.8	25.9	27.7	0.4
Toluene	—	—	20.2	Toluene	—	—	—	—
Naphthalene	—	8.8	7.1	Naphthalene	—	—	—	—
Others	—	—	8.7	Others	—	3.7	1.5	37.3
Total benzene conversion (per gram catalyst)	3.5	7.5	42.0	Total benzene conversion (per gram catalyst)	5.0	8.0	17.5	13.5

[a] Reaction conditions: volume ratio ethylene/helium: 5/95; volume ratio propylene/helium: 6/94; benzene pressure p_B: 200 Torr; ethylene pressure p_E: 28 Torr; propylene pressure p_P: 36 Torr; molar ratio benzene/ethylene: 7.0/1; molar ratio benzene/propylene: 5.6/1; activation temperature t_A: 450°C; velocity of flow: 30 ml/min.; mass of the catalyst sample: 0.2 g.

to $t = 0$. In the following sections only these extrapolated values $\varphi(t = 0)$ were used. Nevertheless, the catalyst poisoning remains a serious problem in the study of the present system, since the conversion φ_E of ethylene (to polyethylene) and the conversion of ethylene to ethylbenzene are of approximately the same order. It is very probable that olefin polymerization causes the poisoning. As has been shown by ir spectroscopic (*32*) and gravimetric (*33*) measurements, a certain amount of ethylene and propylene is irreversibly held by H-mordenite. The rate of the polymerization process was determined by comparing the gas-chromatographic ethylene peak of the feed gas with the corresponding peak of the output, increased by certain amounts due to the ethylene, which had gone into the products (ethylbenzene, diethylbenzene). It was found that the rate of polymerization under the conditions of the alkylation reaction and under ethylene pressures between 0 and 40 Torr is directly proportional to the ethylene concentration (Fig. 3). Thus, the conversion φ_E to polyethylene is independent of the ethylene pressure [$\varphi_E \propto r_R/c_0$(ethylene); see Eq. 2]. This made it possible to account for the losses of ethylene caused by polymerization by studying the dependence of the reaction rate on ethylene pressures (see

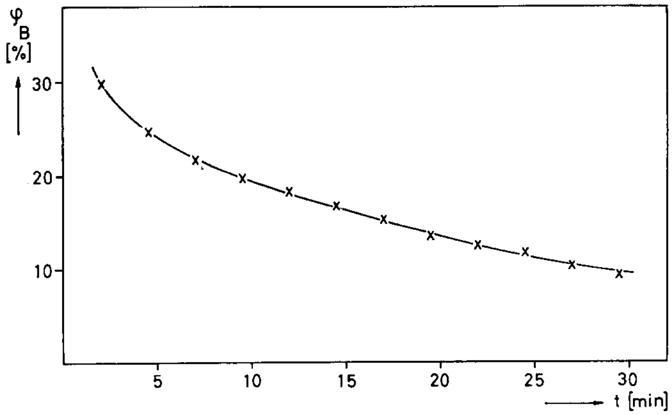

FIG. 2. The time dependence of benzene conversion φ_B (in percent per gram catalyst).

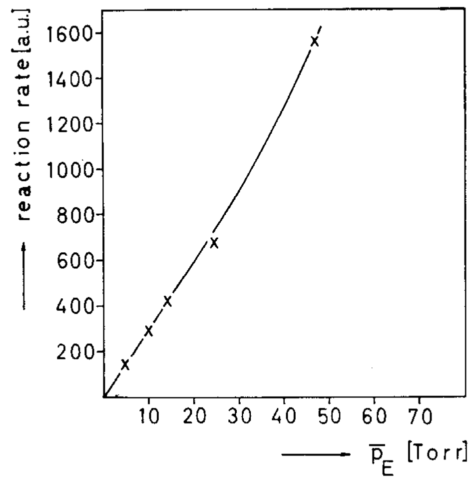

FIG. 3. Reaction rate of ethylene (to polyethylene) in arbitrary units as a function of the mean pressure of ethylene under the conditions of the alkylation reaction.

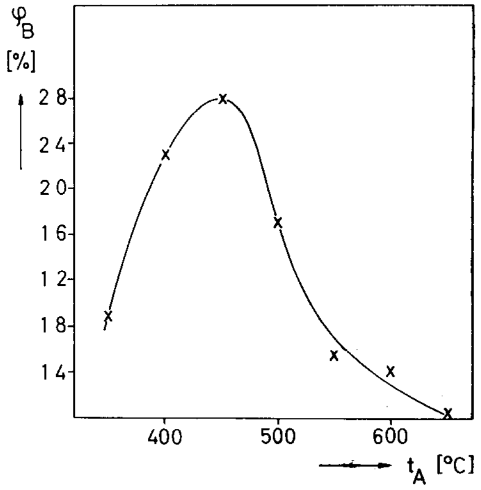

FIG. 5. Conversion of benzene (φ_B) to ethylbenzene (in percent per gram catalyst) as a function of the activation temperature (t_A) of catalyst (H-mordenite).

below). The influence of temperature on the polymerization (percent turnover of ethylene to polymers) is shown in Fig. 4. Though the absolute rate of polymerization obviously increases up to 200°C, it was observed that the lifetime of the catalyst was higher at higher temperatures. This probably results from better regeneration of the active centers at elevated temperatures. However, it is an open question, as to whether coke deposits at higher temperatures may also influence the activity of the catalyst. Furthermore, φ_E was found to be a constant above 200°C for various conditions which possibly indicates that the rate determining step is the growth of chains rather than their initiation.

Effect of Activation Temperature and Olefin Dilution by Helium

Figure 5 shows the dependence of benzene conversion on the temperature of activation. These measurements were carried out with undiluted ethylene and benzene at equal partial pressures at t_R =

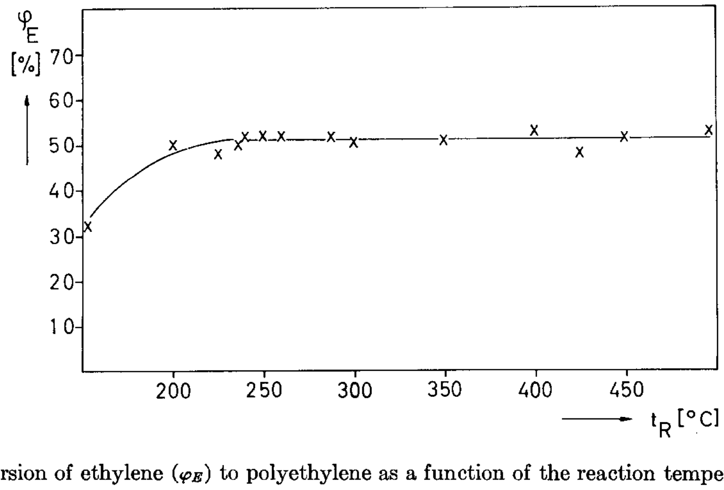

FIG. 4. Conversion of ethylene (φ_E) to polyethylene as a function of the reaction temperature (t_R) under the conditions of the alkylation reaction.

102°C. A distinct maximum of activity appears for an activation temperature of $t_A = 450°\text{C}$. When these experiments were repeated using an ethylene/helium mixture (2 vol % ethylene; $p_E = 11.3$ Torr, $p_B = 200$ Torr, $p_{He} = 547.7$ Torr, $t_R = 150°\text{C}$) a maximum activity again appeared at an activation temperature of 450°C. Since the absolute amounts of $\varphi_B(t)$ were remarkably higher in the latter case, it follows that dilution of the ethylene with helium increases the lifetime of the catalyst by decreasing the degree of poisoning by polymerization. Since 450°C had turned out to be the optimum for activation, we pretreated the catalyst throughout all the later experiments at this temperature.

Effect of Reaction Temperature on the Conversion of Benzene

The benzene conversion $\varphi_B(t = 0)$ was measured as a function of reaction temperature between 100 and 500°C. An ethylene/helium mixture with 2 vol % ethylene was used, to reduce the polymerization, thus making it possible to obtain a benzene/ethylene molar ratio of 18. The results are presented in Fig. 6. Here, it is seen that the benzene conversion decreases over 300°C. Thus, it is not worthwhile to study the reaction above 300°C because at higher temperatures other products are formed in addition to ethylbenzenes (see first section). Furthermore, above a reaction temperature of $t_R = 350°\text{C}$ the reverse process, i.e., the cracking of the ethylbenzenes begins to play a role (*34*).

For the Arrhenius plot in Fig. 7, results from the two next sections had to be used, i.e., especially Eq. (3), where α and β were 0.6, which were determined at 150°C. Since there is no indication of a change in the mechanism these data should be applicable even for higher reaction temperatures. This was checked for α at 400°C ($\alpha \approx 0.7$). However, the use of these α and β values means only a slight correction for the temperature dependence of the reactant concentrations. A variation of α and β between 0.2 and 1.5 would cause a change of the apparent activation energy of 15% only. The fact that the circled point at 423 K does not exactly fit the straight line is presumably due to the increase of the rate of the parallel polymerization between

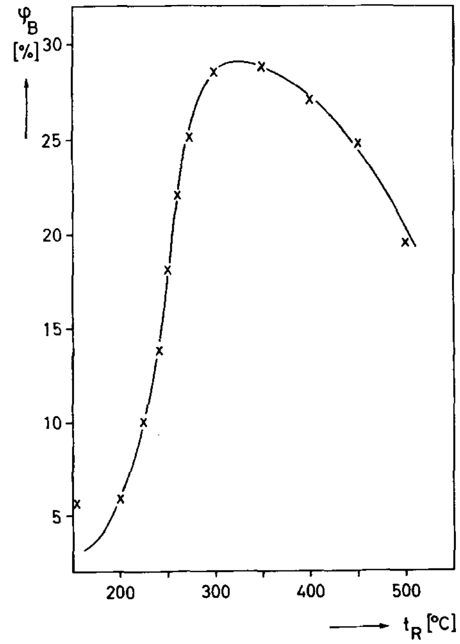

Fig. 6. Conversion of benzene (φ_B) to ethylbenzene (in percent per gram catalyst) as a function of the reaction temperature (t_R).

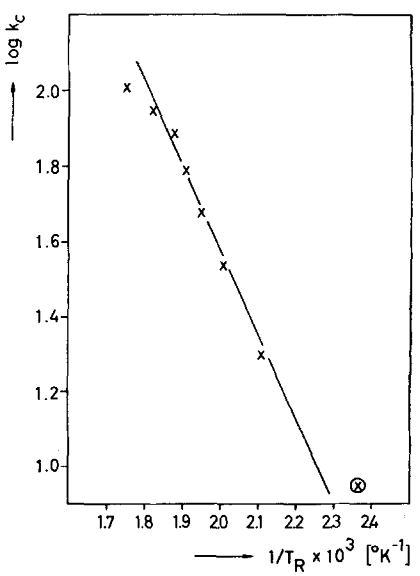

Fig. 7. Arrhenius plot for the alkylation of benzene with ethylene.

150° and 200°C (see Fig. 4). From the Arrhenius plot (Fig. 7), one obtains an activation energy of 10 kcal/mole.

Effect of Ethylene Pressure p_E on the Conversion of Benzene

In order to vary the ethylene pressure, mixtures of ethylene and helium with 1 to 15 vol % ethylene were used. The pressure of benzene was held constant at 200 Torr. In these experiments and in those in the next section, the reaction temperature was 150°C. As can be seen from Fig. 8, the conversion $\varphi_B(t = 0)$ reaches a maximum when the pressure of ethylene is about 30 Torr.

Effect of Benzene Pressure p_B on the Conversion of Benzene

For these measurements, a gas mixture containing 1 vol % ethylene and 99 vol % helium was used. The benzene pressure was varied by appropriately adjusting the temperature of the evaporator. Since a constant total pressure was maintained, the ethylene pressure decreased slightly when the benzene pressure was increased. Furthermore, the conversion φ_B was not simply proportional to the reaction rate r_m, since c_0 (benzene) $\propto p_B$ [see Eq. (2)], which made it more difficult to evaluate the results. Firstly, it has been assumed that the kinetics may be sufficiently described by the relation

$$r = kp_E{}^{\alpha}p_B{}^{\beta}. \qquad (3)$$

Secondly, α was determined ($\alpha = 0.6 \pm 0.04$) from the ascending part of the curve in Fig. 8. Finally, Eqs. (2) and (3) were combined to give

$$\frac{\varphi_B}{p_E{}^{0.6}} = k'p_B{}^{\beta-1}. \qquad (4)$$

A value of $\beta = 0.6 \pm 0.1$ was deduced by using Eq. (4) and the slope of the log–log plot of the data shown in Fig. 9.

Discussion

It has been shown by P. Venuto *et al.* (*10*) that the reaction of benzene and ethylene leads to higher alkylated products, when faujasite-like zeolites (Linde X, Linde Y) are used as catalysts. This seems to be reasonable because the orifices of these molecular sieves (diameter ca. 9 Å) are sufficiently large. In contrast, mordenite contains channels with an access opening that is only slightly larger than the size of the benzene molecule. Therefore, this catalyst should permit only those molecules to be formed whose critical diameters do not exceed significantly those of benzene. Excellent agreement with this suggestion was obtained in our experiments because only ethylbenzene, *m*-diethylbenzene, *p*-diethylbenzene, cumene, *p*-diisopropylbenzene, and *m*-diisopropylbenzene were detected, but no *o*-dialkylbenzenes and no higher alkylated products; *o*-di-

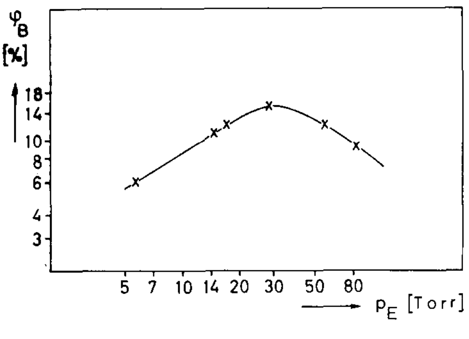

FIG. 8. Conversion of benzene (φ_B) to ethylbenzene (in percent per gram catalyst) as a function of the ethylene pressure (p_E).

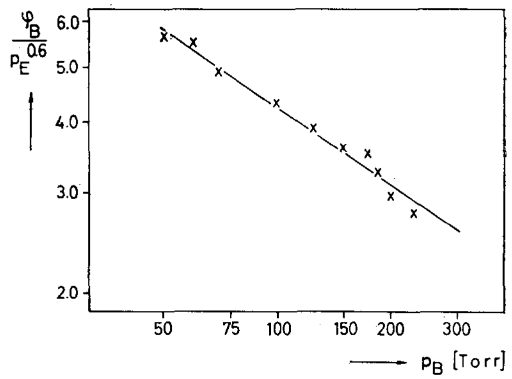

FIG. 9. Conversion of benzene (φ_B) to ethylbenzene (in percent per gram catalyst), corrected for variation of the ethylene pressure p_E, as a function of the benzene pressure (p_B).

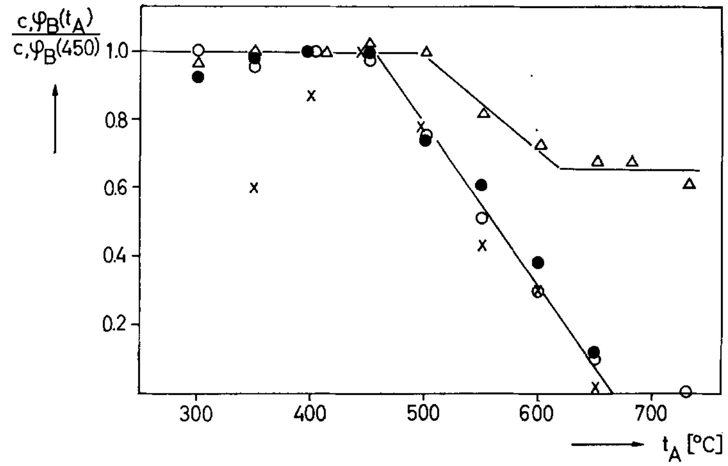

FIG. 10. Correlation between the concentrations c of Brønsted centers (○), OH groups (●), Lewis sites (△), and conversion of benzene (φ_B) to ethylbenzenes (×) as a function of the temperature of activation (t_A). The concentrations of sites of the mordenite catalyst were obtained using ir spectroscopy (*29*). All the data were normalized for the values corresponding to t_A = 450°C.

ethylbenzene should have been detected by our technique if its amount exceeds 0.1%. By analysis of a test mixture of *o*-, *m*-, and *p*-diethylbenzene it was determined that our column was able to resolve these three components. The size of *o*-diethylbenzene is slightly unfavorable and its formation is stericly hindered. Furthermore, Olah *et al.* (*35*) have pointed out that the equilibrium concentrations of *o*-diethylbenzene (and *o*-diisopropylbenzene) are very small. They found the following equilibrium composition (in mole %) at 300 K: 3 *o*-diethylbenzene; 69 *m*-diethylbenzene, and 28 *p*-diethylbenzene. Now, it is well known that isomerization of alkylbenzenes is also catalyzed by zeolites (*36*). Therefore *o*-diethylbenzene, which may be originally formed, would very rapidly transform to *p*- and *m*-diethylbenzene. Furthermore, the formation of naphthalene may occur via *o*-diethylbenzene (*31*) (see above).

The ratio of *m*- and *p*-dialkylbenzenes is markedly changed when propylene is used instead of ethylene for alkylation (see Table 1).† Even though the formation of *m*-diisopropylbenzene is thermodynamically preferred, just as that of *m*-diethylbenzene. [Equilibrium composition at 300 K in mole %: 0 *o*-diisopropylbenzene, 68 *m*-diisopropylbenzene, 32 *p*-diisopropylbenzene (*35*).] But the dimensions of *m*-diisopropylbenzene (9.0 Å × 7.4 Å × 6.3 Å) do not sufficiently fit the diameters of the mordenite channels. So the product composition is preferably determined by the steric factor. In general, the experimental results up to 300°C are an excellent proof of the selectivity for benzene alkylation with olefins, as was expected for the mordenite catalyst on the basis of its special crystal structure. S. Csicsery (*37, 38*) has pointed out that the very same explanation applies to the shape selectivity of H-mordenite in transalkylation and disproportionation of alkylbenzenes.

The activity of the mordenite catalyst reaches its maximum after activation at 450°C (see Fig. 5). The question then arises as to whether this result can be explained by a parallel temperature dependence of the concentration of active sites. An attempt has been made to decide this problem by measuring the concentrations of the possibly active centers (acid OH Brønsted groups, Lewis sites) as a function of temperature. This was carried out with ir spectroscopy (*29*). The ir results are compared with the activity dependence in Fig. 10. It is evident from Fig. 10 that there is a good

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† This is in agreement with earlier results of similar investigations of K. A. Becker and U. Köckeritz.

correlation between activity and concentration of Brønsted sites from 450°C (optimum activation temperature) to about 670°C. At approximately 650°C, the activity has nearly vanished, the OH concentration has dropped to ca. 8% but that of the Lewis centers is still 66% of the maximum. Thus, it can be concluded that the Brønsted sites are of decisive importance for the catalytic mechanism. The fact that the activity has a lower value below 450°C, while the concentration of active places remains unchanged, is easily understood as follows: one has to take into account that at these temperatures small amounts of adsorbed water (detectable by an ir band at 1640 cm^{-1}) still remain in the pores of the zeolite. This residual water prevents the hydrophobic reactants (benzene, ethylene) from reaching the active sites but does not hinder the motion of the hydrophilic molecules of pyridine, which are used as indicators for Brønsted and Lewis sites.

The measurements of the temperature dependence of the benzene conversion yields a surprisingly low apparent energy of activation (10 kcal/mole). At first, it might seem obvious to explain this result by assuming that the rate-controlling process is diffusion within the zeolitic pores. On the other hand, some arguments seem to contradict this assumption:

(i) the variation of the primary particle size by a factor of ten (2.5–25 μ in diameter) exhibited no influence upon the reaction rate
(ii) the apparent activation energy of the diffusion of hydrocarbons like methane, ethane, benzene, and cumene in mordenite only amounts 1.5 to 2.0 kcal/mole (*39*, *33*)
(iii) the P. Weisz's criterion (*40*) for nondiffusion-controlled reactions in porous catalysts was fulfilled in the present case which may for our purposes be written as follows

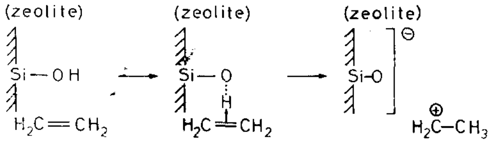
$$(R_0^2/D)(u/v_0)(c_0/c_s)\varphi_B < 3 \qquad (5)$$

With our experimental data,

R_0 (mean radius of the particles) = 3.5×10^{-4} cm,
D (diffusion coefficient of benzene, measured vs adsorption) = 10^{-10} cm^2/sec (*33*, *39*),
u (velocity of flow) = 0.5 cm^3/sec,
v_0 (volume of the catalyst) = 0.6 cm^3,
c_0 (input concentration of benzene) = 1.5×10^{-5} mole/cm^3,
c_s (surface concentration of benzene) = 7×10^{-3} mole/cm^3 (*33*), and
φ_B (benzene conversion) = 10% per gram,

the left-hand side of expression (5) is about 0.2.

Furthermore, Topchieva *et al.* (*5*) obtained a similar low value of the apparent activation energy (7.6 kcal/mole) for the alkylation of benzene with propylene over LaY. Like LaY, the H-mordenite catalyst is one of the most active zeolites. Hansford and Ward (*13*) have shown by comparison of various zeolites (MgX, CaY, MgY, REY, HY, and H-mordenite) that the isomerization of *o*-xylene is catalyzed best by H-mordenite. So the low value of the apparent activation energy for the alkylation of benzene with ethylene over H-mordenite (10 kcal/mole) seems to be reasonable. It is in the order of that, necessary for proton transfer in OH group containing minerals¶ (*42*). Therefore, it seems to be possible that a similar process is the rate controlling step during the alkylation of benzene on H-mordenite:



Nevertheless, the authors feel that further work is needed to decide, whether diffusion is involved in the rate determining process. Especially studies on the adsorption of reactant mixtures are highly desirable. The rate of the reaction can be described by Eq. (3) as has been shown by the experiments for pressures up to 30 Torr for ethylene and 200 Torr for benzene (see Fig. 8 and Fig. 9). The question then arises as to whether the exponent α in Eq. (3) is influenced by the parallel polymerization of

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¶ In the case of goethite (FeOOH), Gallagher *et al.* (*41*) obtained 8.3 kcal/mole.

ethylene. On the other hand, the measurements of the polymerization rate under the conditions of the alkylation reaction have shown (see Fig. 3) that the conversion of ethylene to polymers is independent of the ethylene pressure and amounts ca. $\varphi_E(t = 0) = 0.3$. This means that only 70% of the feed ethylene is available for the alkylation process. However, the only consequence to the evaluation of the experimental data is a parallel shifting of the curve log $\varphi_B(p_E)$ in Fig. 8, which leaves the exponent α unchanged. One can easily show for the same reason (φ_E = const. within the pressure region mentioned above) that the reactor is differentially working with respect to the alkylation reaction even though the conversion of ethylene is relatively high (*34*).

It has been suggested by P. Venuto *et al.* (*4*) that the alkylation of benzene, by means of zeolites catalysts, may occur by a Rideal mechanism. However, in this case one of the reactants, e.g., ethylene, must be adsorbed at certain activating sites, the other reactant is unbonded and impinges from the homogeneous phase. Since the diameters of the penetrating molecules and those of the zeolitic pores are comparable, no molecule within the pores can be considered as being free and without interaction with the solid. Therefore, it is possible that the maximum in Fig. 8 may indicate a Langmuir–Hinshelwood type mechanism. This would require both reacting species to be adsorbed. Of course, they should not be chemisorbed at the same type of sites, for instance at Brønsted groups, since then both species would simultaneously become slightly positive in charge (*4*). However, it is possible that the molecules of ethylene and benzene may be adsorbed on adjacent but different places (*33*, *34*) and the benzene molecules may partially hinder the ethylene species to reach the activating sites.

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