ETHYLBENZENE CRACKING ON AN AGING H-MORDENITE CATALYST

By
A. BECKER and W. STELLMACH
Berlin-West

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In accordance with the "Time-on-Stream-Theory" for the cracking of ethylbenzene four different reaction models have been discussed. They differ in the number of active sites involved in the cracking and poisoning reaction step. The apparent activation energies of the partial reactions have been determined.

Introduction

The H-forms of zeolites, particularly H-mordenite, present a high catalytic acitivity for many reactions which occur by a carbonium-ion-mechanism [1—4]. On the other hand this highly active behavior involves sometimes also catalysis of undesirable side reactions, the products of which can act as inhibitors. In the course of such a reaction an increasing self-poisoning will take place. The poisoning is caused by a blocking of the active sites. This uneconomic aging effect has been studied in detail by WOJCIECHOWSKI and co-workers [5—7] in their "Time-on-Stream-Theory".

In the treatment of catalyst decay WOJCIECHOWSKI considered the poison concentration as constant. If the inhibitor is produced by the reaction itself, however, its concentration is a function of conversion and therefore will be time dependent. Cracking of ethylbenzene on H-mordenite is an example for such a situtation.

Experimental procedure

The experiments had to be carried out in such a way that the applied H-mordenite becomes charged only during the actual measurement, because aging of catalyst starts already during the first seconds. A pulse reactor is most suitable for this case.

The experimental arrangement consists mainly of a stainless steel differential flow reactor. At the beginning of a run, 5 mg of the pre-purified catalyst were activated in the reactor tube itself under definite conditions at 500 °C. For this purpose the substance was heated to 500 °C [8] at a rate of 9 deg/min in a He-flow (30 ml/min). After a holding time of 30 minutes the catalyst was cooled down to reaction temperature at a rate of 5 deg/min. After 3 hours the He-flow rate was increased up to 490 ml/min and after one more hour the crack experiments started.

A pulse of 10 µl ethylbenzene was injected by means of a syringe into the He-carrier gas line and after passing the reactor the products were analyzed in a connected gas chromatograph. The reaction temperature was varied in steps of 25 degrees between 300° and 425 °C.

Calculation model

The course of the reaction is determined by the primary cracking reaction at the active sites Z and the poisoning of these sites $Z(t)$. Two assumptions were made:

1) Cracking occurs in a first order reaction and n sites are involved in the initial reaction step

$$A+nZ \xrightarrow{k_R} AZ_n^{\neq} \rightarrow B+P+nZ \tag{1}$$

A means the initial reactant, B a product and P is also a product molecule, which additionally acts as an inhibitor. Because the reaction takes place in a differential reactor, during the reaction of the pulse the concentration of A can be considered as constant with sufficient approximation, *i. e.*

$$\frac{dx_A}{dt} = k_R[Z]^n. \tag{2}$$

2) In the poisoning process one adsorbed inhibitor molecule P occupies m active sites

$$P+mZ \xrightarrow{k_P} PZ_m^{\neq} \rightarrow PZ_m. \tag{3}$$

Therefore the poisoning reaction is determined by the concentration of P and that of possibly present impurities P' of the initial reactant A. Assuming $c_P \sim x_A$ and $c_{P'} \sim c_A^0$,

$$c_{P,\text{total}} = c_P + c_{P'} = a(c_A^0 - c_A) + bc_A^0.$$

Taking $b/a = \eta$; $c_{P,\text{total}} = a \cdot c_A^0(x_A + \eta)$

$$-\frac{d[Z]}{dt} = k_P a \cdot c_A^0[Z]^m \cdot (x_A + \eta) \tag{4}$$

Solving the system of equations (2), (4) for different values m and n in order to find the time dependent degree of conversion $x_A(t)$ is cumbersome. If it is necessary to assume parallel reactions at energetically different sites, as in our case, no explicit solution can be found. Because the selected experimental conditions, however, are those of a differential reactor, a different way of solution is possible.

During the passage of the pulse through the catalyst material the concentration of active sites $[Z]$, determining the conversion x_A, decreases according to equ. (4). Dividing the pulse into a large number (>700) of sufficiently small elements allows one to consider $[Z]$ in equ. (2) as well as $[Z]$ and x_A on the right side of equ. (4) as constant within close integration limits. For a better approximation, the conversion in equ. (4), which increases during the passage time t_R of the pulse element i from 0 to x_i, is taken to be the mean value $x_i/2$. The pulse element is chosen as the free volume v_0 of the catalyst material. Therefore, at a pulse v_P this volume can be divided

in $v_P/v_0 = i_M$ elements. The total conversion of the first pulse found by gas chromatography thus results in a mean value of i_M partial conversions

$$^1x_A = \frac{1}{i_M} \sum {}^1x_i .$$

The superscript is related to the pulse number. To avoid double indices in the following A is omitted.

The evaluation of the experimental data showed that a satisfying curve fitting, especially for the first pulses, can be achieved only by assuming two energetically different sites Z and Z'. The total conversion ${}^\mu X$ of the pulse μ therefore is

$$^\mu X = {}^\mu x + {}^\mu x' .$$

${}^\mu x$ is determined by k_P, k_R and $[Z_0]$ whereas ${}^\mu x'$ by k'_P, k'_R and $[Z'_0]$. Under the stated assumptions and considering that in equ. (4) x has to be replaced by $x + x' = X$ integration of equs. (2) and (4) yields for the first element of the first pulse

$$^1x_1 = k_R [^1Z_0]^n t_R$$

and

$$^1x'_1 = k'_R [^1Z'_0]^n t_R \tag{5}$$

respectively.

After the passing of this element the initial concentration of sites has decreased to $[^1Z_1]$ and $[^1Z'_1]$ respectively:

$$\begin{aligned} [^1Z_1] &= [^1Z_0]\left\{1 - \frac{1}{2} k_P a c_A^0 [^1Z_0]^{m-1} (^1X_1 + 2\eta) t_R\right\} \\ [^1Z'_1] &= [^1Z'_0]\left\{1 - \frac{1}{2} k'_P a c_A^0 [^1Z'_0]^{m-1} (^1X_1 + 2\eta) t_R\right\}. \end{aligned} \tag{6}$$

Simplifying the notation by the substitutions

$$\Omega_m = \frac{1}{2} k_P a c_A^0 t_R [^1Z_0]^{m-1}$$

$$\Omega'_m = \frac{1}{2} k'_P a c_A^0 t_R [^1Z'_0]^{m-1}$$

$$^1Y_1 = 1 - \Omega_m (^1X_1 + 2\eta)$$

$$^1W_1 = 1 - \Omega'_m (^1X_1 + 2\eta)$$

$$^1Y_i = 1 - (^1Y_{i-1}^{m-1} - {}^1Y_{i-1}^m)(^1X_i + 2\eta) : (^1X_{i-1} + 2\eta)$$

$$^1W_i = 1 - (^1W_{i-1}^{m-1} - {}^1W_{i-1}^m)(^1X_i + 2\eta) : (^1X_{i-1} + 2\eta)$$

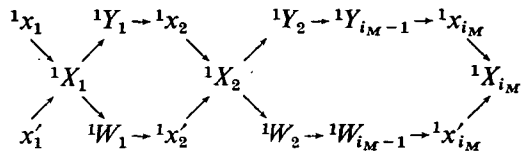
gives

$$\begin{aligned} ^1X_1 &= {}^1x_1 + {}^1x'_1 \\ ^1X_2 &= {}^1x_1 {}^1Y_1^n + {}^1x'_1 {}^1W_1^n \\ &\vdots \quad\quad \vdots \quad\quad \vdots \\ ^1X_i &= {}^1x_{i-1} {}^1Y_{i-1}^n + {}^1x'_{i-1} {}^1W_{i-1}^n . \end{aligned}$$

For the first element of the later pulses μ,

$$ {}^{\mu}x_1 = {}^{\mu-1}x_{i_M}\,{}^{\mu-1}Y^{n}_{i_M} \quad \text{and} \quad {}^{\mu}x'_1 = {}^{\mu-1}x'_{iM}\,{}^{\mu-1}W_{i_M} $$

is valid accordingly. Therefore ${}^{1}X=\frac{1}{i_M}\sum {}^{1}X_i$ can be calculated easily with a computer using the following calculation scheme:



(7).

The needed input quantities ${}^{1}x_1$, ${}^{1}x'_1$, Ω_m, Ω'_m and η in case of primary reactant poisoning are found by fitting the experimental data.

Results and discussion

The cracking conversion as a function of pulse number and reaction temperature has been evaluated from the amount of benzene formed. According to the calculation scheme (7) the optimal curve fittings $X=X(\mu, T_R)$ for $m=1$ or 2 and $n=1$ or 2 were determined. The best fitting resulted for $m=2$ and $m=1$ and is shown in Fig. 1. The ethylbenzene used was extremely pure having been fractionated in a gas chromatograph. Therefore $\eta=0$ in (6) was justified.

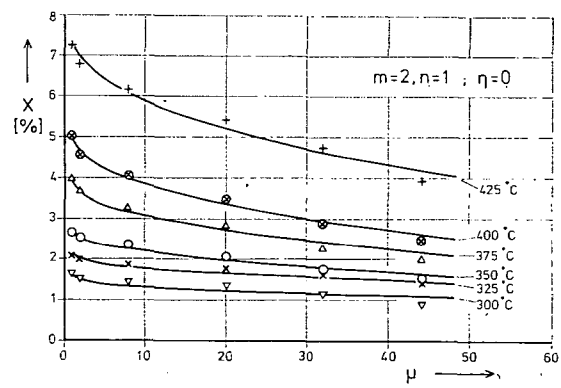


Fig. 1. Conversion of ethylbenzene over H-mordenite at different temperatures as a function of pulse number. The solid lines are calculated for $m=2$ and $n=1$

To test the chosen reaction model ($m=2$; $m=1$) cracking experiments were evaluated in which 0.1, 1, and 2% of pyridine had been added to the ethylbenzene as an inhibitor. The experimental and calculated curves are illustrated in Fig. 2 and show good correspondence.

For the determination of the apparent activation energy E_R for the primary cracking reaction at the sites Z_0 equation (5) is applied, in which the temperature dependent quantities (${}^1x_1$, k_R and t_R) yield the Arrhenius equation:

$$\ln ({}^1x_1 \cdot T_R) = -E_R/R \cdot 1/T_R + \text{const.} \tag{8}$$

Fig. 3 shows the result giving $E_R = 13$ kcal/mol. An analogous plotting of $\ln ({}^1x_1' \cdot T_R)$ yields $E_R' = 9$ kcal/mol. These apparent activation energies have to be added to the heat of adsorption of ethylbenzene (about 15 kcal/mol) to get the true activation energies.

For the determination of the activation energy of the poisoning reaction E_P, equ. (6) has to be applied, which leads to

$$\ln (\Omega_2 \cdot T_R^2) = -E_P/R \cdot 1/T_R + \text{const.} \tag{9}$$

Fig. 4 shows the Arrhenius diagramm, which results in 5.9 kcal/mol for E_P. By analogy, with Ω', 2.1 kcal/mol for E_P' is found.

In spite of the relative low activation energy found for the cracking, the reaction does not seem to be influenced by diffusion. This follows from the fact that no dependence of conversion on crystal size (about 0.2 to 30 μm) has been found. Besides, no increase of activation energy with increasing pulse number has been found, which should be the case if diffusion hindrance is rate determining.

For the course of the cracking reaction on H-mordenite according to the analysis of the assumed reaction models the following statements seem to be valid: The reaction is of first order (related to ethylbenzene) and there is always one site ($n=1$) in-

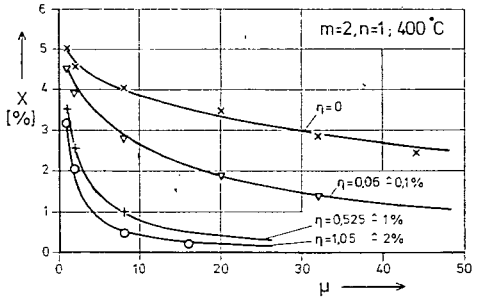


Fig. 2. Conversion of ethylbenzene over H-mordenite at 400 °C for different amounts of catalyst poison added as a function of pulse number. The solid lines are calculated for $m=2$, $n=1$ and η as indicated

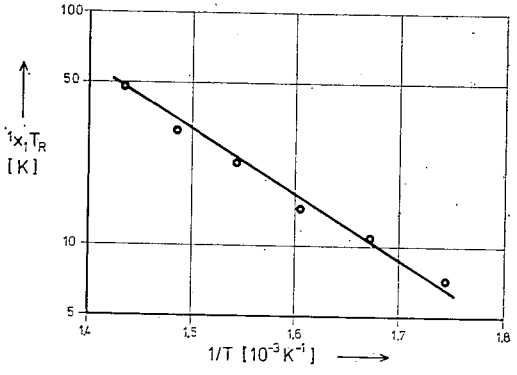


Fig. 3. Arrhenius plot for the cracking reaction

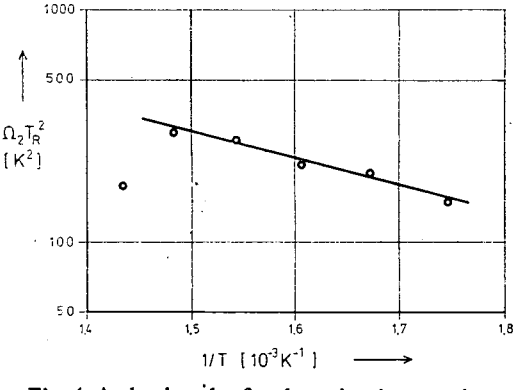


Fig. 4. Arrhenius plot for the poisoning reaction

volved in the initiating rate determining reaction step. Simultaneously a self poisoning of the catalyst takes place: one adsorbed product molecule is able to block two active sites ($m=2$).

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