

KINETICS OF ETHYLBENZENE HYDROGENOLYTIC DEALKYLATION ON Ni-Al₂O₃ CATALYST

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Kinetic equation was found for dealkylation of ethylbenzene at the presence of hydrogen on a Ni-Al₂O₃ catalyst at 330°C which indicates a complicated course of this vapor phase catalytic reaction. Similar character of reaction course showed also the demethylation of toluene on the same kind of catalyst and at the same reaction conditions. These results differ from results obtained for this reaction previously.

In the years 1961 – 1970, this Laboratory has paid a great attention to hydrogenolytic reactions and particularly to hydrogenolytic dealkylation of aromatic compounds. Kinetics of hydrogenolytic demethylation of toluene and all three isomers of xylenes on a Ni-Al₂O₃ catalyst was published by Setínek and coworkers¹. At a high level of statistical probability, the course of all investigated reactions was possible to describe with a series of Langmuir–Hinshelwood kinetic equations from which one was selected for comparison of demethylation rate of the studied compounds. It was found that toluene and *p*-xylene demethylation rates are comparable and the lowest rate showed *o*-xylene. This fact was interpreted by the steric hindrance of the methyl group in the *ortho* position.

The technical grade xylene mixture contains besides toluene also certain amount of ethylbenzene and therefore we measured the kinetics of its hydrodealkylation at the same reaction conditions and on the same type of catalyst as was used in the above cited paper.

The determination of ethylbenzene kinetics complements the knowledge of further component of the industrial C₈ hydrocarbon fraction and gives information on kinetics and mechanism of ethyl group splitting from the aromatic nuclei.

EXPERIMENTAL

Materials. Hydrogen (electrolytic) Bitterfeld, G.D.R. Nitrogen (bulb) Technoplyn, Ostrava, Czechoslovakia, was purified on a deoxidizing catalyst at 400°C and dried by molecular sieve 5A. Ethylbenzene was rectified to chromatographic purity.

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Catalyst. Preparation procedure was as described in the previous paper¹. Composition of the catalyst was NiO 28.6 wt. %, Al₂O₃ 26.7 wt. % and humidity 44.7 wt. %. Specific surface area BET was 294 m²/g.

Apparatus. Liquid ethylbenzene was injected at the required rate into a glass, electrically heated evaporator (180°C) using linear syringe pump (Vývojové dílny ČSAV). Hydrogen and nitrogen in required molar ratio to ethylbenzene were introduced into the evaporator and their feeding rate was measured by differential flowmeters. This arrangement enabled variations of the reaction mixture flow rate and assured required molar ratio of reaction components. The preheated feed was introduced into a glass tube reactor; the upper part was packed with glass balls for adjusting the reaction mixture to the required temperature and in the lower part, the catalyst (0.2–0.5 g) was placed. The reactor was heated by an electrical furnace which temperature was regulated so that the thermocouple located in the middle of the catalyst bed indicated the desired reaction temperature. All kinetic experiments were made at 330°C. Reaction products leaving the reactor were cooled in a condenser to –78°C.

Procedure. The catalyst was activated in the reactor with hydrogen at 400°C for 1 hour, then the temperature was lowered to 330°C and after that the reaction mixture was fed at the desired rate F (mol/h). For every experiment, a new portion of the catalyst was used.

Analytical method. The liquid reaction product was analyzed by gas chromatography on a column 3 000 × 3 mm packed with Chromosorb W with 5% of a mixture of Bentonit 34 and dinonylphthalate (2 : 1) at 72°C. Flame ionization detector and nitrogen as carrier gas were used.

RESULTS AND DISCUSSION

In accord with our earlier experience from the investigation of hydrogenolytic reactions, the experimental set-up used assures that the kinetic data obtained were free of influence both of external and internal diffusion.

Recently, Teichner and coworkers² investigated the hydrogenolysis of ethylbenzene on a Ni–Al₂O₃ catalyst. They have found that the hydrogenolytic dealkylation of ethylbenzene proceeds on a Ni catalyst by consecutive splitting of side chain carbons in the form of methane, i.e. according to the reaction mechanism proposed for the dealkylation of alkylbenzenes earlier^{3,4}.

Analysis of the non-condensing part of reaction products confirmed that during the dealkylation of ethylbenzene only methane is produced. Ethane was not found. The consecutive mechanism is probably effective due to the substantial differences in the bond energies which for the bond between the benzene nucleus and the ethyl group is 368 kJ/mol whereas for the bond CH₃—CH₂C₆H₅ in the ethylbenzene molecule is 264 kJ/mol (ref.⁵).

Using the initial reaction rate method, the kinetics of only the first reaction of the supposed mechanism, i.e. splitting of methyl group from the rest of the ethylbenzene molecule, could be determined. The rate was estimated as the disappearance of ethylbenzene which equals to the sum of moles of toluene and benzene formed. It was verified experimentally that in the range of low conversions (to 7 mole %), the conversion is linearly proportional to the space time and the value of initial reaction rate can be calculated from the relation $r^0 = x/(W/F)$, where r^0 is initial reaction

rate ($\text{mol h}^{-1} \text{kg}^{-1}$), x is fractional conversion of ethylbenzene, W is weight of catalyst (kg) and F is rate of ethylbenzene feeding (mol/h).

In some experiments, the initial catalytic activity was decreasing gradually with time but at most after three hours it became stabilized to a constant value. For the kinetic measurement the data obtained after 4 hours of catalyst work were used.

The measurements were performed at three different values of partial pressure ratios of hydrogen and ethylbenzene $p_{\text{H}}^0/p_{\text{EB}}^0 = 1, 4$ and 9 . For each of these values, the initial reaction rates of dealkylation for five different values of partial pressure of ethylbenzene were determined. The adjustment of ethylbenzene concentrations was realized by dilution of the reaction mixture by nitrogen. The dependences of initial reaction rates of ethylbenzene dealkylation on its partial pressures are presented in Fig. 1. It can be seen that all dependencies have a maximum which is more pronounced with the increase of the ratio $p_{\text{H}}^0/p_{\text{EB}}^0$ and at the same time the position of the maximum is shifted to lower values of p_{EB}^0 .

The experimental data were processed by the nonlinear regression using Marquardt's algorithm⁶. The sum of squared relative errors $Q = \sum ((r_{\text{calc}}^0 - r_{\text{exp}}^0)/r_{\text{exp}}^0)^2$ was minimized. At the beginning, we tried to correlate all the kinetic data obtained using a broad collection of Langmuir-Hinshelwood kinetic equations developed with the supposition that surface reaction of ethylbenzene and hydrogen is the rate

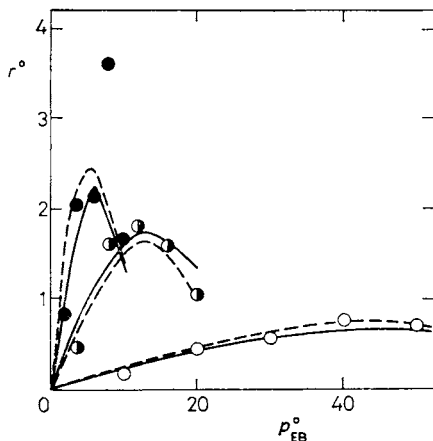


FIG. 1

Dependence of initial reaction rate r^0 ($\text{mol h}^{-1} \text{kg}_{\text{cat}}^{-1}$) of ethylbenzene dealkylation on ethylbenzene initial partial pressure p_{EB}^0 (kPa). ----- Dependence calculated by Eqs (1)–(3) (Table I), ——— dependence calculated by Eq. (5) (Table II)

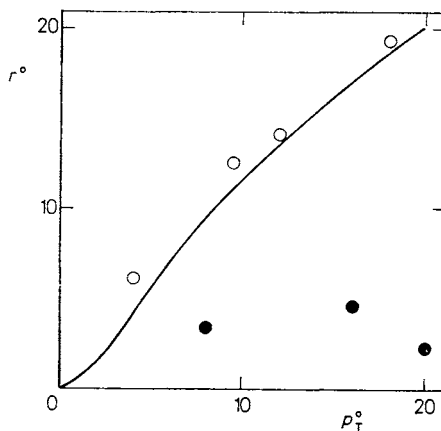


FIG. 2

Dependence of initial reaction rate r^0 ($\text{mol h}^{-1} \text{kg}_{\text{cat}}^{-1}$) of toluene dealkylation on toluene initial partial pressure p_{T}^0 (kPa). \circ Data obtained by Pecev and Setínek¹
 \bullet ($p_{\text{H}}^0/p_{\text{T}}^0 = 4$)

determining step. But with this type of kinetic equations (e.i. with both partial pressures of ethylbenzene and hydrogen in the numerator), it was not possible to fit the data with adequate accuracy. Therefore we tried to process individual parts of experimental data (corresponding to individual values of p_E^0/p_{EB}^0 ratio) separately. The reaction rate values obtained in this case were in better agreement with the course of experimental data (dotted lines in Fig. 1); the best results were obtained with equations presented in Table I. The numerical values of coefficients in numerators of these equations are nearly directly proportional to the ratios of initial ethylbenzene and hydrogen partial pressures whereas the values of coefficients in the denominators of these equations are near to the squares of these ratios.

This shows what kind of adjustment the kinetic equations require in order to achieve over-all correlation with experimental data in the whole range of reaction conditions used. The most important is evidently a change of the kinetic term in the numerator of kinetic equation. The relation of coefficients in Eqs (1) to (3) (Table I)

TABLE I

Kinetic equations for ethylbenzene hydrodealkylation at fixed values of the ratio p_H^0/p_{EB}^0

No.	Equation	p_H^0/p_{EB}^0
(1)	$r^0 = 0.0021p_{EB}^0p_H^0/(1 + 0.00018p_{EB}^0)^3$	1
(2)	$r^0 = 0.0096p_{EB}^0p_H^0/(1 + 0.0030p_{EB}^0)^3$	4
(3)	$r^0 = 0.0256p_{EB}^0p_H^0/(1 + 0.0136p_{EB}^0)^3$	9

TABLE II

Kinetic equations for ethylbenzene hydrodealkylation valid in the whole range of reaction conditions

No.	Equation	Q
(4)	$r^0 = 0.00290p_H^{02}/(1 + 0.0179p_H^0 + 0.0p_{EB}^0)^3$	2.35
(5)	$r^0 = 0.00289p_H^{02}/(1 + 0.0165p_H^{02} + 0.0163p_{EB}^0)^3$	0.49
(6)	$r^0 = 0.00254p_H^{02}/(1 + 0.0434p_H^{02} + 0.0456p_{EB}^0)^{8.06}$	0.44
(7)	$r^0 = 0.103p_H^{02}p_{EB}^0/(1 + 0.049p_H^0 + 0.214p_{EB}^0)^3$	2.00
(8)	$r^0 = 0.0021p_H^{02}/(1 + 0.0157p_H^0 + p_{EB}^0)^3$	0.81
(9)	$r^0 = 0.00173p_H^{02}/(1 + 0.00957p_H^{02} + 0.0p_{EB}^0)^3$	2.74

to the ratios of partial pressures of ethylbenzene and hydrogen suggests that the numerator should contain the square of hydrogen partial pressure only. With a series of this type of kinetic equations we have tried to correlate the complete set of experimental data. The results are summarized in Table II.

The lowest value of the sum of squared errors Q have been obtained with Eqs (5) and (6). The high value of the exponent in the denominator of Eq. (6) is a result of calculation when the value of this exponent was optimized as the fourth coefficient of the kinetic equation.

Only rate equations (5) and (6) have shown adequate agreement between the calculated and experimentally found reaction rate data. This fact shows the dominant influence of partial pressure of hydrogen on the course of the reaction studied and only a slight contributin of partial pressure of ethylbenzene.

This form of kinetic equation is rather unusual for bimolecular catalytic reactions. It is not possible to derive this type of kinetic equation under the assumption of a single rate determining step in the mechanism of the catalytic reaction. However, it is interesting that the same type of kinetic equation have been found by Kraus and coworkers⁷ in the case of toluene dealkylation on a nickel-molybdenum-alumina catalyst. On the other hand, our present results differ substantially from the kinetics of toluene and xylene hydrodealkylation presented by Setínek and coworkers¹ even though they were obtained under the same conditions and on analogical catalyst. For this reason, we have measured the kinetics of toluene hydrodealkylation as well, but the results of these measurements have confirmed the results presented in this paper regarding both the character of dependence of reaction rate on toluene partial pressure (at constant value of p_H^0/p_T^0) and the reaction rate values found (Fig. 2).

Kinetic equations which we have developed are probably only an empirical approximation of much more complicated mechanistic relations. They have been obtained in relatively narrow range of reaction conditions. For the deeper insight into the kinetic description of this type of catalytic reactions, an additional study should be made in much broader range of partial pressures and temperatures than was possible in our experimental set-up.

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