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The Disproportionation of Toluene over a HY/β-AlF$_3$/Cu Catalyst

2. Kinetics

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A catalyst containing 72 wt% HY zeolite, 18 wt% β-AlF$_3$, and 10 wt% Cu was used in a kinetic study of the vapor-phase disproportionation of toluene into benzene and xylenes. The kinetic data were adequately described by three Hougen–Watson rate models of the general form:

$$r = \frac{k_o \exp(-E/RT)(P_T - (P_B \cdot P_X/K_e)^{\frac{1}{2}})}{1 + K_{H_2,o} \exp(\Delta H_{H_2}/RT) P_{H_2}{}^n + K_{c,o} \exp(\Delta H_c/RT) P_T P_{H_2}{}^m},$$

where n is either $\frac{1}{2}$ or 1 and m can take values of 0, $\frac{1}{2}$, or 1. It was demonstrated that benzene had no effect on the rate whereas xylenes retarded it.

NOMENCLATURE

Symbol	Description
B, T, X, M	Benzene, toluene, xylenes, methane
c	Reaction complex
E	Activation energy (cal/mol)
E_a	Apparent activation energy (cal/mol)
k	Reaction rate constant (g mol/g·s·atm)
K	Adsorption equilibrium constant (atm^{-1})
K_e	Thermodynamic equilibrium constant
P	Partial pressure (atm)
r	Reaction rate (g mol/g·hr)
S	Selectivity
W/F	Space time (g·hr/mol)
Y_D	Yield
ξ	Degree of conversion
Π	Total pressure (atm)
k_o	Frequency factor

INTRODUCTION

Very little of the large body of published information on the disproportionation of toluene into benzene and xylene deals with the kinetics of the reaction. Izumi and Shiba (*1*), as well as Ogawa *et al.* (*2*) and Iwamura *et al.* (*3*), identified the surface reaction as the rate-determining step. The value of −1.0 kcal/mol for the heat of adsorption of toluene in Ogawa and Iwamura's rate equation seems rather low in view of the fact that chemisorption is very likely under their experimental conditions. None of the above-mentioned authors corrected their data for the effect of catalyst deactivation on the rate of reaction. Yashima's studies on H mordenite (*4*) took the rather pronounced catalyst deactivation into account by using the reaction rates extrapolated to zero time on stream. Since the initial catalyst activity was invariably high, the rates obtained in this manner were also high and it is therefore not surprising that

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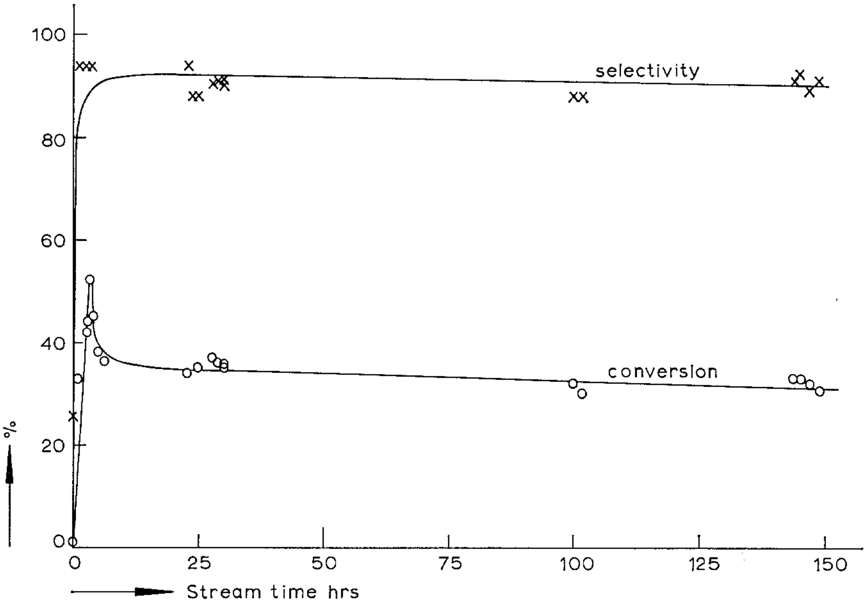

FIG. 1. Performance of catalyst AB1. $T = 500°C$; $\Pi = 10$ atm; W/F = 177 g cat·hr/mol toluene; H_2/toluene = 16.7 mol/mol.

above 350°C pore diffusion was the rate-determining step: above this temperature, the apparent activation energy decreased to 11.8 kcal/mol from the value of 18.8 kcal/mol determined below 350°C. Yashima found a zero-order dependence of the rate on the partial pressure of toluene and ascribed this to the strong adsorption of toluene on the catalyst.

In this paper, the kinetics are studied for the HY/β-AlF_3/Cu catalyst (18 wt% β-AlF_3 and 10 wt% Cu) previously described (*5*). Hydrogen was used as diluent in all experiments in order to minimize catalyst deactivation. First, some preliminary experiments are described in order to demonstrate the influence of the process variables on the reaction rate. Then initial reaction rates are determined at 400 to 500°C and at 2.0 to 11 atm total pressure. One set of the rate determinations was carried out by varying the partial pressures of the two feed components, hydrogen and toluene, simultaneously. This was accomplished by keeping the hydrogen/toluene ratio constant at 16.7 mol/mol and varying the total pressure. Another set of experiments was performed at varying hydrogen/toluene ratios and total pressures in order to determine the effect of hydrogen partial pressure on the rate. The effect of the disproportionation products, benzene and xylenes, was also investigated.

The results have been used to establish a kinetic model for the toluene disproportionation reaction.

EXPERIMENTAL

Materials. The toluene, analytical grade, was used without further purification. Chemically pure hydrogen was dried over molecular sieves 3A and passed over reduced copper on silica (BASF R3-11 BTS) catalyst to remove traces of oxygen and other impurities.

Equipment. The kinetic measurements were carried out in a standard continuous flow apparatus.

Hydrogen was purified from oxygen and water and metered by a flow controller. Dry and deaerated aromatics were fed by Hughes micrometering pumps to an evaporator. The stainless-steel reactor (30 cm long, 1-cm internal diameter) was placed in a fluidized bed, which made it possible to control the reactor temperature to within ±1°C.

Product samples were separated in a chromatographic column containing bentone and diisodecylphthalate on Chromosorb W and analyzed by flame ionization detection.

Procedure. For the kinetic experiments, a catalyst bed of 30-cm length, containing 15 to 20 g catalyst, particle size 0.21 to 0.42 mm, was used. These dimensions are such that a good approach to plug flow was assured. Calculation also showed that, under the conditions of the experiments, neither pore nor film diffusion limited the rate of toluene disproportionation.

The catalyst was activated according to the procedure previously described (*8*). Three reactions account for the components present in the product, viz.:

$$2T \rightleftarrows B + X \quad \text{(toluene disproportionation)}$$

$$T + H_2 \rightarrow B + M \quad \text{(hydrodealkylation of toluene)}$$

$$2X \rightleftarrows T + TMB \quad \text{(xylene disproportionation)},$$

where M, T, B, X, and TMB denote methane, toluene, benzene xylenes (equilibrium ratios), and trimethylbenzenes (also present in equilibrium ratios). From these reactions expressions for the conversion of toluene (ξ) and disproportionation selectivity (S) can be derived as was shown in a previous paper (*8*). The expressions for the yield of products by toluene disproportionation alone is given by:

$$Y_D = \frac{2(Y_X + 2Y_{TMB})100}{Y_B + Y_T + Y_X + Y_{TMB}}\ \%,$$

where Y_B, Y_T, Y_X, and Y_{TMB} stand for the mole fractions of benzene, toluene, xylenes, and trimethylbenzenes, respectively.

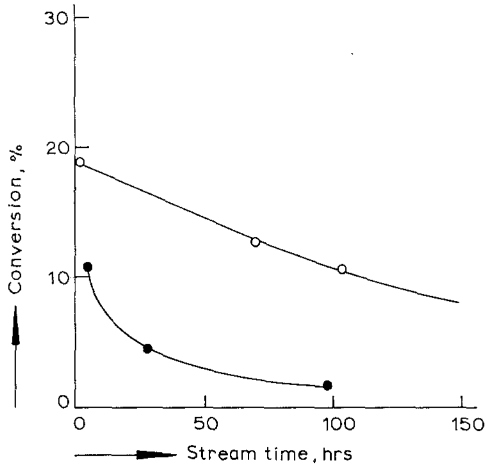

FIG. 2. Influence of H_2/toluene ratio on catalyst deactivation. $T = 500°C$; $\Pi = 1.1$ atm; W/F = 177 g cat·hr/mol toluene. ○, H_2/toluene = 16.7 mol/mol; ●, H_2/toluene = 0 mol/mol.

RESULTS

Preliminary experiments. Experiments at fixed pressure, temperature, hydrogen/toluene ratio, and space velocity (see Fig. 1) showed that initially catalyst activity increased to a maximum value at about 3 hr stream time and then decreased, rapidly at first and more gradu-

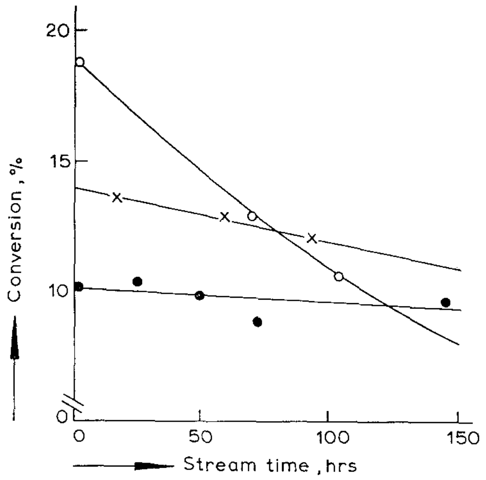

FIG. 3. Influence of total pressure on catalyst deactivation. $T = 500°C$; W/F = 177 g cat·hr/mol toluene; H_2/toluene = 16.7 mol/mol. ○, $\Pi = 1.1$ atm; ×, $\Pi = 3$ atm; ●, $\Pi = 6$ atm.

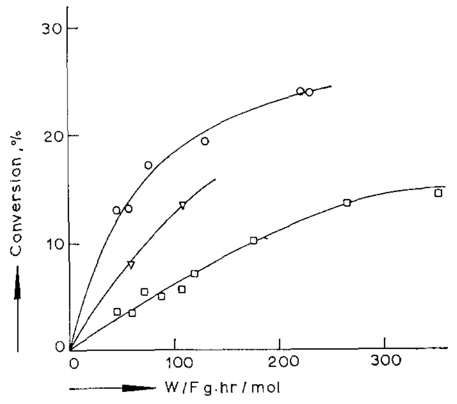

FIG. 4. Variation of conversion as a function of space time at 500°C and H_2/toluene = 16.7 mol/mol. ○, Π = 105. atm; ▽, Π = 6 atm; □, Π = 3 atm.

ally later. At the same time, catalyst selectivity went through a minimum, then increased to more than 90%.

Although the kinetic measurements were performed during the period of slow deactivation and high selectivity, a correction for loss of activity during the slow deactivation was applied. To this end, the yield Y_D was measured at the end of each experimental run at one standard condition ($P = 6$ atm, $T = 450°C$, H_2/toluene = 16.7 mol/mol, and W/F = 177 g·hr/mol). The yields obtained at the standard conditions were observed to be well described by a straight line:

$$Y_s = A - B \cdot t,$$

where Y_s is the yield at standard conditions, A and B are constants and t is the stream time in hours. This relationship was used to correct for deactivation during the kinetic runs by normalizing the measured yields to a standard activity level corresponding to 9.5% yield, which is the average of the yields observed at standard conditions:

$$Y = \frac{9.5 Y_m}{Y_s},$$

where Y is the corrected yield, Y_m is the measured yield which is to be corrected, and Y_s is calculated from Eq. (1) by substituting the stream time in hours at which Y was measured.

After a modification of the equipment which made it possible to work with a diluent, experiments with mixtures of argon and hydrogen (Fig. 2) as diluent gas confirmed that hydrogen diminishes catalyst deactivation. At constant total pressure and constant toluene partial pressure, deactivation was faster in the absence of hydrogen.

Figure 3 shows that higher total pressures also minimize catalyst deactivation. At a constant hydrogen/toluene ratio, the rate of deactivation decreased as the total pressure increased and became all but negligible at 6 atm and a 16.7-mol/mol hydrogen/toluene ratio.

The effect of hydrogen and toluene partial pressures on the reaction rate was investigated qualitatively in the prelimi-

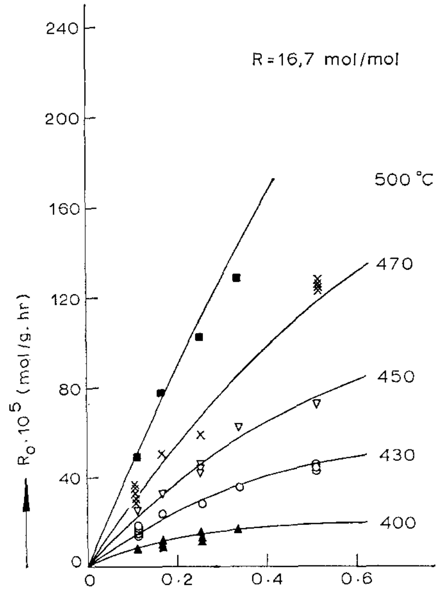

FIG. 5. Initial rates of toluene disproportionation as a function of toluene partial pressure. H_2/toluene = 16.7 mol/mol. Points: measured data; lines: calculated from Model 1 of Table 2.

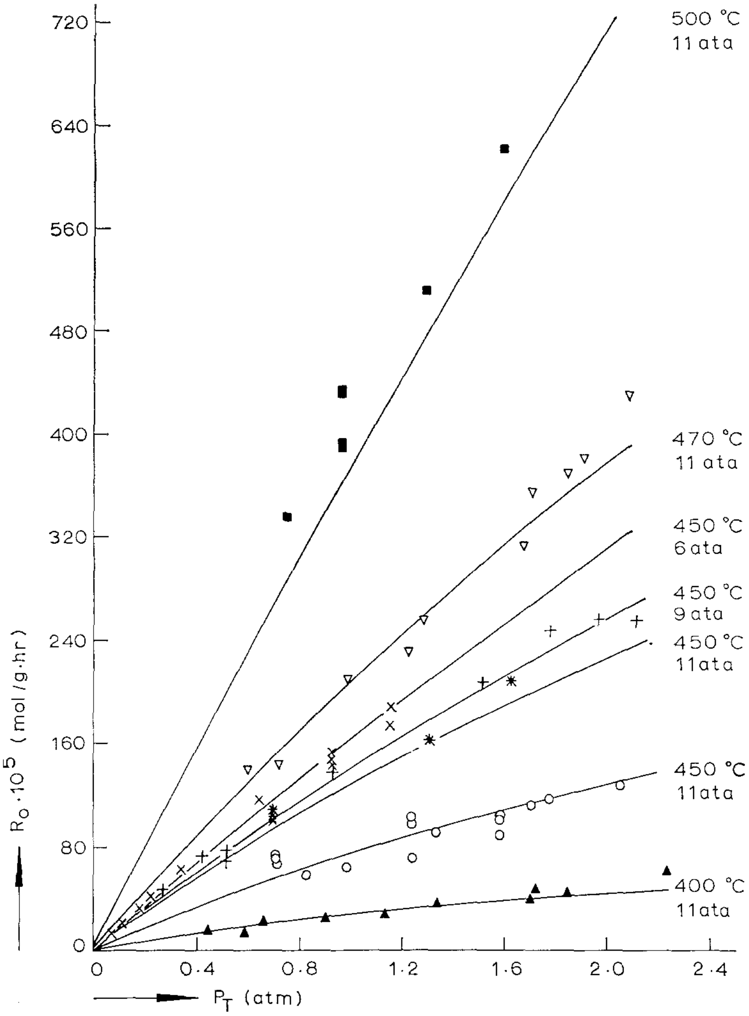

FIG. 6. Initial rates of toluene disproportionation as a function of toluene partial pressure. H_2/toluene = 3 to 80 mol/mol. Points: measured data; lines: calculated from Model 1 of Table 2.

nary experiments. First, the hydrogen partial pressure was varied while the total pressure and the toluene partial pressure were constant. This was realized by partially replacing hydrogen by argon at constant total gas flow rate. The results indicated a definite influence of hydrogen partial pressure on the rate. At low hydrogen partial pressures, the disproportionation rate corrected for deactivation decreased rapidly with increasing hydrogen partial pressure, but the rate became independent of this variable, within experimental accuracy, at higher partial pressures. On the other hand, the rate increased consistently with increasing toluene partial pressure.

Kinetic measurements. The variation of toluene conversion with space time (Fig. 4) shows a definite curvature at higher conversions. It appears, however, that for conversions below 10% the reactor may be considered differential. Assuming that at such low conversions, benzene and xylenes do not influence the rate of toluene disproportionation, the initial rate r_0 can

TABLE 1

Apparent Activation Energy, E_a, as a Function of Pressure

Π (atm)	P_T (atm)	E_a (kcal/mol)
2.0	0.113	19.0
3.0	0.169	19.9
4.5	0.254	20.5
6.0	0.339	21.4
9.0	0.509	25.3

be calculated from

$$r_o = \frac{Y_D}{W/F_{toluene}},$$

where Y_D is the yield of disproportionation products and $W/F_{toluene}$ is the modified space time.

In Fig. 5 the initial rates at a constant hydrogen/toluene ratio of 16.7 mol/mol are given as a function of the partial pressure of toluene.

The apparent activation energy of the reaction at different pressures was estimated by making an Arrhenius plot with the data of Fig. 5; the results are summarized in Table 1. The apparent activation energy appears to vary with total pressure. The pressure dependence of the apparent activation energy normally points to a temperature dependence of at least one of the adsorption terms in the reaction rate equation. Figure 6 shows the initial reaction rates measured at varying hydrogen/toluene ratios and temperatures at 11 atm total pressure. At 450°C the total pressure was varied between 6 and 11 atm, from which it is clear that hydrogen has a retarding effect on the rate, as already found from the preliminary experiments.

In order to describe the kinetic results mathematically, Hougen–Watson reaction rate models were derived and applied to fit the experimental data plotted in Figs. 5 and 6. A nonlinear regression computer program based on the modified steepest descent optimization method described by

TABLE 2

Results of the Regression on the Initial Toluene Disproportionation Rate

Model No.	Initial rate, r_o (mol/g·hr)	k_o (mol/g·hr·atm)	E_a (kcal/mol)	$K_{H_2,o}$ (atm^{-1})	ΔH_{H_2} (kcal/mol)	$K_{c,o}$; $K_{T,o}$ (atm^{-2})	ΔH_c; ΔH_T (kcal/mol)	SSQR
1[a]	$\frac{k_o \exp(-E_a/RT)P_T}{1 + K_{H_2}P_{H_2} + K_cP_TP_{H_2}}$	4.43×10^2	17.6	9.67×10^{-11}	−24.8	3.05×10^{-10}	−23.1	1.51
2[a]	$\frac{k_o \exp(-E_a/RT)P_T}{1 + K_{H_2}P_{H_2}^{\frac{1}{2}} + K_cP_TP_{H_2}^{\frac{1}{2}}}$	4.37×10^2	14.0	5.93×10^{-9}	−21.5	2.04×10^{-11}	−29.0	1.54
3[a]	$\frac{k_o \exp(-E_a/RT)P_T}{1 + K_{H_2}P_{H_2} + K_TP_T}$	1.96×10^2	16.4	4.82×10^{-10}	−22.9	2.03×10^{-9}	−26.9	1.52

[a] $K_{H_2} = K_{H_2,o} \exp(-\Delta H_{H_2}/RT)$; $K_c = K_{c,o} \exp(-\Delta H_c/RT)$; $K_T = K_{T,o} \exp(-\Delta H_T/RT)$.

Powell (6) was used. The starting values of the parameters of the various models were estimated by linear regression. The objective function minimized is Q, the sum of squares of the deviations between measured rates, r_{o_i}, and the corresponding calculated rates, r_{c_i}, from each model, weighted with the reciprocal of the squared observed rate:

$$\mathrm{SSQR} = Q_{\min} = \sum_{i=1}^{n} (r_{oi} - r_{ci})^2/r_{oi}^2,$$

where SSQR is the sum of squares of the weighted residuals between measured and calculated rates at convergence.

Totally there were 20 models tested. An F test on the variance (*5*) showed that three models described the kinetic data adequately (see Table 2). Another F test revealed that the difference between the three models is not significant at the 95% confidence level. Hence, from a statistical point of view, it is impossible to say that one of these models describes the data best. The rates calculated with Model 1 are plotted in Figs. 5 and 6.

Influence of reaction products. The effect of the products on the rate was studied by adding either benzene or *m*-xylene to the toluene–hydrogen feed. At temperatures between 400 and 500°C, total pressures between 1 and 10 atm, and a constant hydrogen/aromatics ratio of 16.7 mol/mol, either benzene or *m*-xylene was added in a ratio to toluene of 1:4 (*5*).

Benzene appeared to have no measurable effect whereas *m*-xylene retards the disproportionation rate. Catalyst deactivation is faster in the presence of *m*-xylene than with toluene only. The experiments also reveal that equilibrium among the xylene isomers is rapidly established. Furthermore, the trimethylbenzenes formed when xylenes are present in the reaction mixture can be ascribed entirely to the disproportionation of xylenes and not to the transalkylation between xylenes and toluene.

DISCUSSION

The preliminary experiments established that a high hydrogen/toluene ratio coupled with a high total pressure and therefore a high hydrogen partial pressure are necessary in order to reduce catalyst deactivation. As the kinetic results demonstrate, hydrogen has a definite retarding effect on the rate. This may be due to the adsorption of hydrogen on the catalyst surface or to the formation of a surface complex. The latter possibility would be in agreement with the supposition that the concentration of the surface carbonium ions involved in such reactions (*17*) is diminished.

The present work shows that three models adequately describe the kinetics. Models 1 and 2 assume the adsorption of toluene to be rate-limiting. Model 1 is based on a mechanism postulating molecular adsorption of toluene, molecular adsorption of hydrogen, and formation of a nonreactive surface complex between hydrogen and toluene (*5*). The mechanism from which Model 2 is derived is similar to that of Model 1 except that dissociative adsorption of hydrogen is assumed. Model 3 is obtained from a mechanism in which adsorbed toluene goes through an activated state and is subsequently converted into benzene and xylenes. Here, too, molecular adsorption of hydrogen is assumed but no complex formation, the formation of the activated species being supposed to be rate-determining.

From a purely statistical point of view it is impossible to choose among the models. Nor it is possible from kinetic data alone to identify the nature of the complex and activated species postulated above.

Experiments with reaction products added to the feed have demonstrated that benzene has no measureable influence on the rate of toluene disproportionation. Xylenes, on the other hand, have a negative effect on the rate. The retarding effect of *m*-xylene can be explained by supposing that xylenes are adsorbed competitively on disproportionation sites, thus decreasing the total surface available for toluene disproportionation. That *m*-xylene is adsorbed more strongly than toluene is consistent with the higher basicity of the former compound and the acidic nature of the catalyst. This may also explain our observation that trimethylbenzenes are preferentially formed by xylene disproportionation rather than transalkylation of xylene with toluene, even though the partial pressure of toluene in the feed is much higher than that of the xylenes.

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