SELECTIVE DEHYDROGENATION OF TETRALIN ON ZEOLITES

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The dehydrogenation of tetralin on two zeolite catalysts has been studied, the experiments were planned statistically according to the Orthogonal Central Composite Design. In order to determine the influence of coke deposits, the time-on-stream theory of catalyst decay is applied too.

Приводятся результаты исследования дегидрирования тетралина на двух цеолитных катализаторах. Статические эксперименты планировались согласно Проэкту Ортогонального Центрального Компонента. Для определения влияния отложения кокса были применены теория время на потоке для распада катализатора.

In a preceding paper /1/, we have shown that tetralin is dehydrogenated both on cobalt and nickel modified zeolites type X. It was also noted that the aging of these catalysts was different. So, the aim of this work was to find the optimum conditions for selective dehydrogenation of tetralin through statistical design of experiments /2/. For this purpose, we examined first the aging of the catalysts using the method proposed in Ref. /3/.

The apparatus used consisted of a static bed plug-flow reactor working at atmospheric pressure /1/. The catalysts used were: NO. 1: $Co_{0.48}Na_{0.52}$I Al, Si I-X, FAU and NO. 2: $Ni_{0.50}Na_{0.50}$ I Al, Si I-X, FAU /4/. For the investigation of aging, reaction temperatures (T) of 653, 673 and 733 K were chosen, at each temperature three catalyst-to-reagent ratios (P) were used and the final time-on-stream (t_f) was varied from 6 to 90 min. For the optimization

of the process, experiments were carried out at temperatures 673, 703 and

733 K and space velocities (WHSV) of 90, 120 and 150 min^{-1}. Both liquid and

gaseous products were analyzed by gas chromatography. At the end of each run,

nitrogen was passed for 1/2 hour through the system, at a rate of 50 ml/min

in order to obtain complete reiteration of the data for coke deposits on catalysts.

The regeneration of the catalysts was carried out for 2 h by air at 773 K.

The average conversion of tetralin (Y) was determined from

$$Y = \frac{1}{t_f} \int \dot{Y} \, dt \tag{1}$$

where $\dot{Y}$ is the conversion of tetralin. The expression relating the conversion

in a plug-flow reactor to the time-on-stream (t) /5/, taking into account the

volume expansion and the aging of the catalyst /3/, for the reaction under

investigation was found to be:

$$-(1 + Gt)^{-N} = s \ln/1 - \dot{Y}/ + p(\dot{Y} + \ln/1 - \dot{Y}/) \tag{2}$$

where G and N are the aging constant and the aging exponent, respectively /3/,

while s and p are the model parameters:

$$s = \frac{[T_o]}{P \, t_f \, k_{tet.} \, [S_o]} \tag{3a}$$

$$p = \frac{K_{naph.} [T_o] - K_{tet.} [T_o]}{p \, t_f \, k_{tet.} \, K_{tet.} \, [S_o]} \tag{3b}$$

where $[T_o]$ is the initial concentration of tetralin (atm), $[S_o]$ is the initial

concentration of active sites (m^{-2}). As shown in Ref. /3/, $[S_o] = [S] (1 + Gt)^N$,

$k_{tet.}$ is the rate constant of dehydrogenation, $K_{naph.}$ and $K_{tet.}$ are the ad-

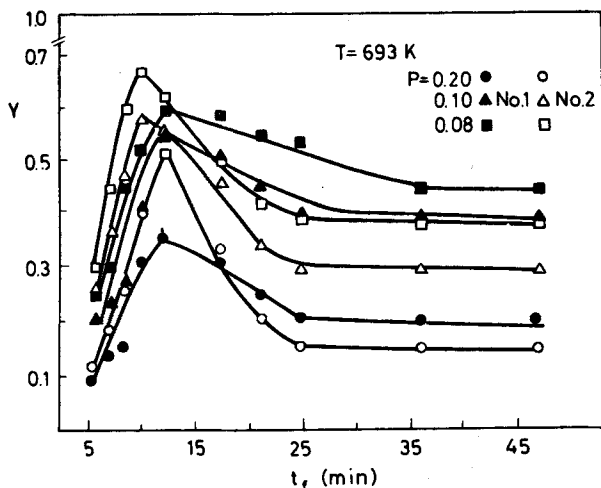sorption equilibrium constants for the reaction components (atm^{-1}).

Fig. 1. Best fit of the experimental data for 693 K with the theoretical model:
/ ■ , ▲ , ● / — for catalyst No. 1, / □ , △ , ○ / — for catalyst No. 2

Thus, the values of Y calculated from eq. (1) were compared with the experimental tetralin conversions for each run.

The experimental results obtained at all the temperatures showed that both catalysts should be of Class III with $N > 1$ /3/. This is why for correlating the data with the theoretical model the estimation of four parameters /G, N, s, p/ is required, which was done using a computer. The criterion of fit was in each calculation the minimum sum of squares of residuals, defined as the difference between the cumulative conversion predicted by the model and that determined experimentally. The theoretical curves obtained using a value of $N = 2$ are shown together with the experimental points in Fig. 1 for one temperature. It is seen that the theoretical model describes the actual aging behavior of the system correctly. If we define θ as the fraction of active sites remaining at time t, then:

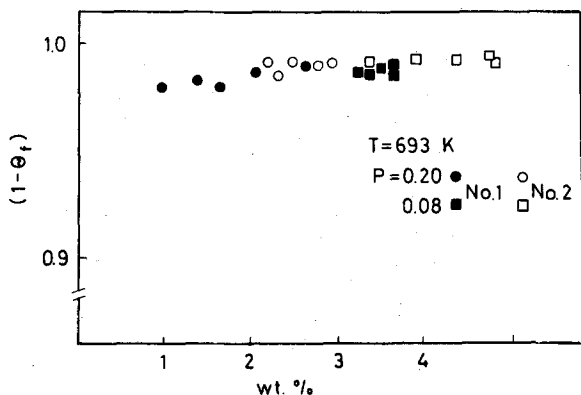$$\theta = \frac{[S]}{[S_o]} = (1 + Gt)^{-N} \tag{4}$$

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Fig. 2. Fraction of active sites lost at the end of a run vs. weight percent coke on the catalyst for data at 693 K. / ■ , ● , / – for catalyst No. 1, / □ , ○ , / – for catalyst No. 2

Thus, the fraction of active sites lost by the end of the run can be given as:

$$(1 - \theta_f) = 1 - (1 + Gt_f)^{-2} \qquad (5)$$

The analysis of $(1 - \theta_f)$ (Fig. 2) showed that the catalytic activity is not directly related to coke on the catalysts. The loss of activity in this case should be connected with the strong adsorption of both reactant and products /1/, so that coke includes species which do not contribute in any way to deactivation. Besides, it was found that after regenerating the catalysts, their original activity was restored.

Thus, having in mind the aging behavior of the catalysts studied, we tried to improve the process for the selective dehydrogenation of tetralin with respect to the percent conversion. For the optimization of the experimental conditions, we correlate two variables: the reaction temperature (x_1) and the space velocity (x_2) with the response function (Y), i.e. the weight percent of tetralin converted, in the form of a polynomial:

$$Y = a_o x_o + a_1 x_1 + a_{12} x_1 x_2 + a_{11}/x_1^2 - \frac{2}{3}/ + a_{22}/x_2^2 - \frac{2}{3} \qquad (6)$$

Table 1

Design Matrix

No.	x_0	x_1	x_2	$x_1 x_2$	$x_1^2 - 2/3$	$x_2^2 - 2/3$	No. 1 exp.	No. 1 pred.	No. 2 exp.	No. 2 pred.
1^z	1	-1	-1	1	1/3	1/3	71	70.96	81	80.24
2^z	1	0	-1	0	-2/3	1/3	85	83.55	90	90.82
3^z	1	1	-1	-1	1/3	1/3	93	94.80	92	92.40
4	1	-1	0	0	1/3	-2/3	55	54.20	81	82.33
5^z	1	0	0	0	-2/3	-2/3	66	66.55	95	93.66
6	1	1	0	0	1/3	-2/3	78	77.55	96	95.99
7^z	1	-1	1	-1	1/3	1/3	45	45.12	76	74.12
8	1	0	1	0	-2/3	1/3	57	57.20	85	86.50
9	1	1	1	1	1/3	1/3	68	67.96	90	89.50

(Table header spans: "Level of variables" over $x_0, x_1, x_2, x_1 x_2, x_1^2-2/3, x_2^2-2/3$; "Conversion Y (wt.%)" over No. 1 and No. 2 columns.)

^{z}Experiments repeated for estimating the experimental error

where $x_0 = 1$, a_0 is calculated from the expression:

$$a_0 = \bar{a} - \frac{2}{3} a_{11} - \frac{2}{3} a_{22}$$

a_1 and a_2 are the coefficients characterizing the influence of the variables, a_{11} and a_{22} are the coefficients characterizing the quadratic effects, the effect of interaction of variables are given by coefficient a_{12}. The design matrix and the results of the experiments carried out under specified conditions are given in Table 1. The values of the coefficients in eq. (6) were determined by the

method of least sqaures. Substituting the round off values of the coefficients, eq. (6) becomes for catalyst NO. 1:

$$Y = 66.55 + 11.67 x_1 - 13.17 x_2 + 0.25 x_1 x_2 - 0.67 x_1^2 + 3.83 x_2^2 \qquad (7)$$

and for catalyst NO. 2:

$$Y = 93.66 + 6.83 x_1 - 2.16 x_2 - 0.75 x_1 x_2 - 4.50 x_1^2 + 5.00 x_x^2 \qquad (8)$$

The comparison of the deviation with the experimental error by the F-test revealed that eqs. (7) and (8) can be used to predict the conversion of tetralin with good accuracy for any set of experimental conditions within the range of the variables studied. Thus, the highest Y for a given t_f using catalyst No. 1 could be obtained at T = 738 K and WHSV = 84 min^{-1}, while for catalyst No. 2, at T = 713 K and WHSV = 228 min^{-1}. The optimum values were then confirmed by experiments and it was found that the caluclated and experimental values were in close agreement.

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