KINETICS OF THE CATALYTIC HYDRODESULPHURISATION REACTION SYSTEM; HYDROGENATION OF ETHYLENE AND BUTENE

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Hydrogenation has been studied of ethylene and butene in a circulation flow reactor on a cobalt–molybdenum catalyst at 360°C and under atmospheric pressure. The effect has been investigated of simultaneous hydrodesulphurisation of thiophene on the hydrogenation. The results have confirmed that different active sites for hydrogenation and hydrodesulphurisation must be considered in the kinetic description of simultaneous hydrogenation of ethylene and hydrodesulphurisation of thiophene. For isolated hydrogenation of ethylene and butene the absence of hydrogen sulphide in the reaction mixture considerably enhances the hydrogenation activity of the catalyst due to the change of its state.

In the previous paper[1] it has been shown that for the kinetic description of hydrogenolysis on a cobalt–molybdenum catalyst different active sites must be considered for the reaction of thiophene than for that of butene, which is an intermediate. The aim of this work has been to verify the concept of different hydrodesulphurisation and hydrogenation sites in case that the reaction of thiophene is accompanied by hydrogenation of another olefin (ethylene). Also, the aim has been to elucidate mutual interference of hydrodesulphurisation and hydrogenation.

EXPERIMENTAL

The experimental method, apparatus with the circulation flow reactor (CSTR), reduction and sulphidation of the cobalt–molybdenum catalyst Cherox 36—00, as well as the method of testing stability of the catalytic activity, have been described in the previous paper[1]. The reader can find there also the method of determination of the amount of hydrogen sulphide in the reaction mixture and the relationships for calculation of partial pressures and rates of formation of hydrogen sulphide and butane.

Chromatographic analysis of saturated and unsaturated hydrocarbons (ethylene, ethane, butene, butane) has been carried out separately for hydrocarbons C_2 and C_4. The analysis conditions for hydrocarbons C_4 have been presented previously[1]; to separate ethylene from ethane a Porapak Q (80—100 mesh) filled column (1·5 m long, 3 mm I.D.) was used. The flow rate of the carrier gas (hydrogen) was 25 cm^3/min at 30°C with flame-ionization detection. Both analyses were carried out from two simultaneously drawn samples of the reaction mixture (0·3 cm^3). On completion of analysis thiophene was flushed from the column by reversing the

flow of the carrier gas. After verification of the linear relationship between the peak area of ethylene and ethane and the injected amount (the slope of the straight line was the same for ethylene and ethane), the conversion was computed from the ratio of ethylene peak area to the sum of peak areas of ethylene and ethane. A reactor balance was used in the following form to calculate the rate of disappearance of ethylene ($-R_E$)

$$-R_E = x_E/(W/F_E) \tag{1}$$

RESULTS AND DISCUSSION

Isolated Hydrogenation of Ethylene and Butene

During kinetic measurements of isolated hydrogenation of ethylene and butene (360°C, atmospheric pressure) the routine was as follows: After standard reduction, sulphidation and test of catalyst activity through the measurements under standard conditions with thiophene[1], the thiophene in the feed was replaced by ethylene or butene. Conversion of olefin grew rapidly first, later slowly (from 25 to 83% for ethylene and from 10% to 25% for butene) to steady down to a constant value roughly after six hours. During this period hydrogen sulphide was detected at the reactor outlet. The kinetic data were obtained after reaching steady activity and on completion of liberation of hydrogen sulphide. During measurements with 1-butene fast isomerization took place to *cis*- and *trans*-2-butene. Consequently, the composition of isomers was at equilibrium.

Experimental results are shown in Fig. 1. To correlate the rate of hydrogenation of ethylene and butene a Langmuir–Hinshelwood type equation in a more general form was used

$$-R_A = \varkappa p_A^a p_H^b/(1 + K_A p_A)^c , \tag{2}$$

where A = E (ethylene) or U(butene). The justification of the assumption that the adsorption constant of hydrogen need not be considered in the adsorption term, may be apparent from Fig. 1: The value $-R_A/p_H$ is independent of partial pressure of hydrogen and the saturated hydrocarbon. In the calculation of kinetic constants (nonlinear regression) the exponents a, b, c were treated first as adjustable parameters. The found exponents ($a = 1{\cdot}2$; $b = 0{\cdot}96$; $c = 0{\cdot}91$ for butene and $a = 0{\cdot}90$; $b = 1{\cdot}2$ and $c = 1{\cdot}3$ for ethylene) were rounded to $a = b = c = 1$ and the remaining constants were computed for these values. The resulting kinetic equations of isolated hydrogenation thus takes the same form for ethylene and butene

$$-R_A = k_A K_A p_A p_H/(1 + K_A p_A) \tag{3}$$

(A = E, U) compatible with the idea that the limiting step is the reaction of the adsorbed olefine with hydrogen reacting from gas phase of from independent centers.

TABLE I

Isolated Hydrogenation of Ethylene and Butene (Eq. (3))

Alkene A	$k_A K_A$ μmol/g h kPa^2	K_A kPa^{-1}	Q (mmol/g h)^2
Ethylene	239	0·043	172
Butene	17·9	0·078	0·45

TABLE II

The Effect of Hydrogen Sulphide on the Rate of Hydrogenation of Ethylene

Inlet composition mol%			x_E %	$(-R_E)_{exp}$ mmol/g h	$(-R_E)_{cal}$ mmol/g h
E	H	S			
5	95	0	84	20·9	19·8[a]
5	90	5	26	6·6	7·1[b]
5	85	10	25	6·3	6·8[b]

[a] Eq. (3) (isolated hydrogenation); [b] Eq. (6) (simultaneous hydrogenation).

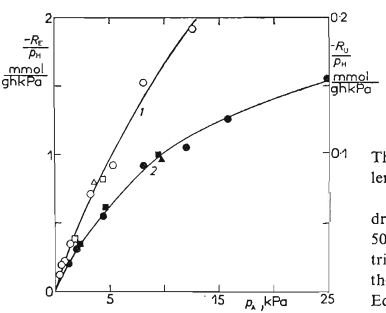

FIG. 1

The rate of Isolated Hydrogenation of Ethylene *1* and Butene *2*

Circles: Only ethylene (butene) and hydrogen present in the feed mixture; squares: 50% of nitrogen added to the feed mixture; triangles: 50% of butane or ethane added to the feed mixture. Curves were computed from Eq. (3).

The computed constants are shown in Table I. The mean relative deviation of experimental reaction rates from computed values (Eq. (3)) is 9% for ethylene and 3% for butene.

In order to ascertain the influence of hydrogen sulphide on the rate of isolated hydrogenation an experiment has been made during which hydrogen sulphide was injected into the feed keeping $W/F_E = 39{\cdot}6$ g hour/mol constant. From Table II it is apparent that the rate of hydrogenation of ethylene significantly drops after the addition of hydrogen sulphide; further increase of the hydrogen sulphide concentration no longer affects the reaction rate. In comparison with the time required to steady down the conversion following the termination of thiophene feeding (approximately 6 hours), the drop of conversion after the onset of hydrogen sulphide injection took place very rapidly (approx. 1/2 hour).

Simultaneous Hydrogenation of Ethylene and Hydrodesulphurisation of Thiophene

Kinetic data (360°C, atmospheric pressure) were obtained in the form of the dependence of the rate of formation of the key component (hydrogen sulphide, butane and ethylene) on the time variable W/F_T for four inlet mixtures ((T/E/H (mol%): 5/5/90; 5/10/85; 10/10/80; 10/5/85). A total of 24 points were obtained.

The rates of formation of hydrogen sulphide, R_S and butane, R_B, were described by the equation from the previous paper[1] (triangular scheme, B−2 model) modified by the terms for adsorption of ethylene $K_E p_E$, $K'_E p_E$)

$$R_S = \frac{(k_1 + k_2) K_T p_T p_H}{1 + K_T p_T + K_S p_S + K_U p_U + K_E p_E}, \qquad (4)$$

$$R_B = [k_2/(k_1 + k_2)] R_S + \frac{k_3 K'_U p_U p_H}{1 + K'_T p_T + K'_S p_S + K'_U p_U + K'_E p_E}. \qquad (5)$$

These equations were derived on the assumption that thiophene reacts to butene on the hydrodesulphurisation sites Z (rate constant k_1). Butane forms predominantly by hydrogenation of butene on the hydrogenation sites Y (rate constant k_3); part of the butane, however, originates directly from thiophene on the sites Z (rate constant k_2). The adsorption constants K_i (Eq. (4)) relate to centers Z, constants K'_i (Eq. (5)) to centers Y. Hydrogen takes part in the reaction from the gas phase or from independent sites, where it adsorbs only weakly.

Equation of the same form as that for isolated hydrogenation of ethylene (3), modified by terms accounting for adospriton of other components, was used to describe hydrogenation of ethylene taking place simultaneously with hydrodesulphurisation of thiophene

$$-R_E = \frac{k_E K'_E p_E p_H}{1 + K'_T p_T + K'_S p_S + K'_U p_U + K'_E p_E} . \qquad (6)$$

This equation is based on the concept that the limiting step is the surface reaction of ethylene adsorbed on the hydrogenation centers Y with hydrogen reacting directly from gas phase or from independent sites.

In the calculation of the constants of Eq. (4) (rate of hydrogen sulphide formation) the set of data was used, containing data on the simultaneous hydrodesulphurisation of thiophene and hydrogenation of ethylene (24 points) together with hydrodesulphurisation of thiophene in the absence of ethylene from the previous paper[1] (53 points). The computed constants (nonlinear regression) and their confidence intervals are summarized in Table III. Eq. (4) describes the rate of formation of hydro-

TABLE III

Constants of Eq. (4) for the Rate of Formation of Hydrogen Sulphide, 77 Experimental Points

Values shown in parentheses pertain to hydrodesulphurisation of thiophene in the absence of ethylene[1], 53 experimental points.

$(k_1 + k_2) K_T$	$12{\cdot}59 \pm 0{\cdot}8$	(12·27)	$\mu mol/g\ h\ kPa^2$
K_T	$0{\cdot}131 \pm 0{\cdot}02$	(0·125)	kPa^{-1}
K_S	$0{\cdot}270 \pm 0{\cdot}04$	(0·249)	kPa^{-1}
K_U	$0{\cdot}031 \pm 0{\cdot}01$	(0·031)	kPa^{-1}
K_E	$0{\cdot}093 \pm 0{\cdot}02$	(—)	kPa^{-1}
Q	2·38	(1·43)	$(mmol/g\ h)^2$

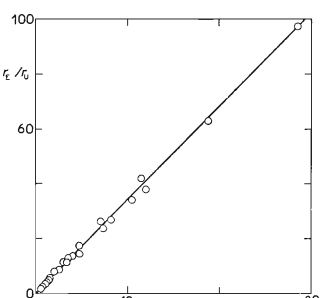

FIG. 2

The Ratio of the Rates of Hydrogenation of Ethylene and Butene during Simultaneous Hydrodesulphurisation of Thiophene

gen sulphide with t e mean relative deviation of 5%. For comparison the table shows also constants of Eq. (4) computed in the previous paper[1], pertaining to hydrodesulphurisation of thiophene in the absence of ethylene. These constants fall into the corresponding confidence limits; both sets are thus statistically indistinguishable. The rate of hydrodesulphurisation (rate of hydrogen sulphide formation) is thus affected by the presence of ethylene only as a consequence of the competitive adsorption on the sites Z ($K_E \neq 0$), where also hydrogen sulphide, thiophene and butene adsorb[2,3].

In the processing of the rates of formation of butane (Eq. (5)) and the rates of disapperance of ethylene (Eq. (6)), we examined first the problem whether hydrogenation of butene and ethylene takes place on the same sites Y. On designating the rate of hydrogenation of butene as

$$r_U = R_B - [k_2/(k_1 + k_2)] R_S \tag{7}$$

we obtain by combining Eqs (5) and (6) the relation

$$r_E/r_U = (k_E K'_E/k_3 K'_U)\, p_E/p_U \tag{8}$$

($r_E = -R_E$), from which it follows that the dependence of the relative reactivity r_E/r_U on the ratio p_E/p_U is linear as long as the hydrogenation of butene and ethylene takes place on the same sites (Y) by the same mechanism. Fom Fig. 2 it is apparent that the experimental values r_E/r_U satisfy this condition. This suggests that Eqs (5) and (6) have the same adsorption terms. This fact has been used in the calculation of constants of Eqs (5) and (6). The constants in both equations were evaluated simultaneously (nonlinear regression); the objective function was

$$Q = w_1 \sum_{i=1}^{n} (R^i_{B,exp} - B^i_{B,cal})^2 + w_2 \sum_{i=1}^{n} (R^i_{E,exp} - R^i_{E,cal})^2 , \tag{9}$$

where n is the number of experimental points, subscripts exp and cal refer to the experimental and calculated values. The statistical weight w_1 and w_2 were adjusted according to the fact that hydrogenation of ethylene is 3·4 times faster than that of butene (the slope of the curve in Fig. 2). Thus $w_1 = 1$ and $w_2 = 1/3{\cdot}4$. The same set of data as that for the rate of hydrogen sulphide formation was used. The calculated constants together with the confidence limits are summarized in Table IV. The rates of butane formation are described by Eq. (5) with the accuracy of 5%; the rates of ethylene disappearance by Eq. (6) with the accuracy of 6%. For comparison the table shows also the constants found in the previous paper[1] by processing the rates of formation of butane in the absence of ethylene. Both sets of constnats are statistically indistinguishable.

From the found values Table III and IV it follows that the adsorption constant of thiophene, hydrogen sulphide and ethylene for hydrodesulphurisation are statistically significantly different from the constants for hydrogenation ($K_T \neq K'_T$, $K_S \neq K'_S$, $K_E \neq K'_E$). While the rate of hydrogenation of butene and ethylene is only slightly affected by the adsorption of ethylene (adsorption of thiophene is without effect $K'_S = 0$ and $K'_T = 0$), the rate of hydrodesulphurisation of thiophene is strongly influenced by the adsorption of hydrogen sulphide, thiophene and ethylene. The results of the kinetic study of simultaneous hydrogenation of ethylene and hydrodesulphurisation of thiophene thus confirm the opinion presented in the previous paper[1] that for the kinetic description different hydrodesulphurisation (Z) and hydrogenation (Y) sites should be considered.

Similar conclusions have reached also Satterfield and Roberts[2] and Lee and Butt[3]. Also Desikan and Amberg[4] consider two types of active sites, although their conclusions are different: The rate of hydrogenation of butene is markedly reduced by the adsorption of thiophene and hydrogen sulphide on the hydrogenation sites.

Comparison of Isolated and Simultaneous Hydrogenation

The rate of isolated hydrogenation of ethylene and butene is markedly higher that the rate of hydrogenation taking place simultaneously with hydrodesulphurisation (Tables I and IV). The explanation that the lowered rate of simultaneous hydrogenation is due to adsorption of thiophene or hydrogen sulphide[4] is in conflict with the kinetic results ($K'_T = 0$, $K'_S = 0$). The marked difference in the rate of hydrogenation of olefins under the isolated and simultaneous course cannot be apparently explained by other means than the change of state of the catalyst: The catalyst which

TABLE IV

Constants of Eqs (*5*) and (*6*) for the Rate of Formation of Butane and Disappearance of Ethylene
Simultaneous hydrogenation and hydrodesulphurisation, 77 experimental points. Values in parentheses pertain to hydrodesulphurisation of thiophene in the absence of ethylene[1], 53 experimental points.

$k_2/(k_1 + k_2)$	0·033 ± 0·01	(0·030)	
$k_3 K'_U$	5·79 ± 0·4	(5·99)	μmol/g h kPa^2
$k_E K'_E$	19·04 ± 2	(—)	μmol/g h kPa^2
K'_T	$0(3 . 10^{-3}) \pm 0{\cdot}003$	$(0(4 . 10^{-4}))$	kPa^{-1}
K'_S	$0(-3 . 10^{-3}) \pm 0{\cdot}003$	$(0(-3 . 10^{-4}))$	kPa^{-1}
K'_U	0 032 ± 0·01	(0·035)	kPa^{-1}
K'_E	0·007 ± 0·002	(—)	kPa^{-1}
Q	1·08	(0·82)	(mmol/g h)^2

is not in contact with hydrogen sulphide (isolated hydrogenation) appears to be in the state of higher activity than under the conditions of hydrodesulphurisation. For a more detailed formulation of this opinion we shall present first some findings from the literature.

It has been known[5] that the state of cobalt–molybdenum catalyst changes in the course of the reduction and sulphidation: A decrease of the coordination of molybdenum takes place and partial (or total) change of oxides to sulphides. Similar changes take place also during hydrodesulphurisation due to the effect of hydrogen and hydrogen sulphide produced by hydrodesulphurisation.

The change of the state of the catalyst takes place even if the injection of thiophene or hydrogen sulphide into the hydrogen feed is terminated. De Beer and coworkers[6] have found that a sulphidated catalyst loses about 1/3 of its sulphur content if it remains in contact with pure hydrogen for about two hours. Interim stoppage of thiophene injection, however, is without effect on the hydrodesulphurisation activity, for sulphur stripped off the catalyst surface is rapidly replenished by hydrodesulphurisation. This "mobil" sulphur, which can be removed by reduction with hydrogen and, on the contrary, replenished by the reaction with hydrogen sulphide, is, according to de Beer, located on the surface of the highly dispersed MoS_2. The observed increase of the hydrogenation activity after termination of thiophene injection (isolated hydrogenation of ethylene and butene) may be associated from this standpoint with the removal of the "mobil" sulphur.

The correlation of the increase of hydrogenation activity with the loss of sulphur from the catalyst surface after termination of the feeding of thiophene or hydrogen sulphide may be explained in terms of the Massoth's model of monolayer[7,8]. According to this model anion vacancies form during reduction, originated by partial stripping of oxygen from the original MoO_3, forming monolayer on the surface of alumina. During sulphidation oxygen is partially replaced by sulphur with corresponding decrease of the number of anion vacancies which become filled by "irreversibly bound" sulphur; in this state the catalyst appears also during desulphurisation. After termination of the supply of thiophene (hydrogen sulphide) the "irreversibly bound" sulphur is removed by reaction with hydrogen which increases the number of vacancies; the observed increase of hydrogenation activity during isolated hydrogenation may be explained by the hypothesis that the active sites are anion vacancies. Also Hedden and Siefried[9] explain increased rate of hydrogenation of propene after termination of the supply of hydrogen sulphide in this manner.

The relation between hydrogenation activity and the number of anion vacancies (the degree of reduction) suggest also the results of Vyskočil and Kraus[10], who observed on a series of cobalt–molybdenum catalysts of different composition reduced under the same conditions the correlation between the hydrogenation activity of cyclohexene with the surface concentration of molybdenum, detected by oxygen adsorption[11].

The fact that not thiophene but hydrogen sulphide reduces hydrogenation activity during simultaneous hydrogenation and hydrodesulphurisation is evidenced by the experiment whose results are shown in Table II. It is apparent that the presence of hydrogen sulphide (independently of its amount) lowers catalytic activity to a level at the simultaneous regime, for the rate of ethylene hydrogenation may be in this case described by Eq. (6) with constants computed from data on simultaneous hydrogenation and hydrodesulphurisation.

LIST OF SYMBOLS

A, T, S, U, B, E	alkene, thiophene, hydrogen sulphide, butene, butane, ethylene
F_i	molar feed rate of component *i*
k	kinetic constant
K_i, K_i'	adsorption constant of component *i*
p_i	partial pressure of component *i*
Q	objective function (summ of squared deviations)
r, R_i	reaction rate, rate of formation of component *i*
W	mass of catalyst
w	statistic weight
x_E	conversion of ethylene
Y	hydrogenation active sites
Z	hydrodesulphurisation active sites

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