KINETICS OF CYCLOHEXENE HYDROGENATION AND OF THIOPHENE HYDROGENOLYSIS OVER COBALT–MOLYBDENUM CATALYSTS OF DIFFERENT COMPOSITION

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The kinetics of the title reactions has been measured at 350°C and atmospheric pressure on six Co—Mo—Al$_2$O$_3$ catalysts prepared by successive impregnation of the support with solutions of molybdenum and cobalt salts and containing these components in different ratios as well as on a commercial Cherox 36—00 catalyst. The activity of these catalysts depended strongly on their composition and showed similar trends for both reactions. Kinetic data were correlated by equations of Langmuir–Hinshelwood type. Their adsorption coefficients have a similar value for different catalysts and all differences in the activity reflected in rate constants. Surface concentrations of molybdenum were determined by low temperature oxygen adsorption and were correlated with experimental rate constants.

Sulphided cobalt–molybdenum catalysts on alumina support, which are widely used in petroleum chemistry, remain still the subject of extensive research. Their complicated chemistry has been reviewed several times[1−3] and original studies continue to appear in the literature. The main problems are: a) the role of cobalt and that of molybdenum, b) the role of support, c) what is the mechanism of hydrodesulphurisation of sulphur compounds on this catalyst, d) whether the active sites for hydrogenation and hydrodesulphurisation are identical or different. None of these problems has been exhaustively elucidated, although the progress in the knowledge is great.

Within the framework of a broader study of hydrodesulphurisation catalysts and processes[4−9], in the present work we were concerned with the problems classified as a) and b), i.e. with the role of cobalt and molybdenum in the formation of active sites for hydrogenation and hydrogenolysis. Our approach was kinetic; on the basis of measurements of the kinetics of model reactions, the hydrogenation of cyclohexene and the hydrogenolysis of thiophene, over a series of catalysts of different composition we tried to find how the form of the rate equations and the values of their constants change with the change in the catalyst composition.

EXPERIMENTAL

Chemicals. Thiophene and cyclohexene were rectified (b.p. 84·1°C and 82·1°C) and their purity was checked by gas chromatography. As on exposure of cyclohexene to light and oxygen peroxides are formed which affect the course of the catalytic reactions, the alkene was stored over sodium; kinetic measurements were then reproducible. Hydrogen and nitrogen were taken from pressure cylinders and freed of oxygen and water (below 10 ppm) by passing them over a bed of a palladium catalyst (hydrogen) or that of a nickel–manganese absorption mass (nitrogen), and further over the bed of silica gel and of A 4 molecular sieve.

Catalysts. As a standard we used a commercial Cherox 36—00 catalyst (Chemické závody, Litvínov). Further prepared were a series of catalysts which were obtained by impregnation of a commercial alumina support Cherox 33—00 (disintegrated to 0·2—0·4 mm particles) by 5% solution of ammonium paramolybdate in 13% ammonia, drying and calcination at 500—550°C, followed by impregnation with 10% cobalt(II) nitrate solution. Then the catalysts were again calcinated at 500—550°C. Their activation by reduction and sulphidation was performed by the following procedure: *1*) raising the temperature to 450°C in a stream of hydrogen and nitrogen (10 : 1); *2*) maintaining the catalyst in a stream of hydrogen at 450°C for 4h ; *3*) then 5 h at 400°C in a stream of hydrogen and hydrogen sulphide (10 : 1); *4*) cooling to room temperature in a stream of hydrogen. Composition of catalysts and their surface (BET) are presented in Table I. Distribution curve of pores obtained by mercury porosimetry showed maxima at 9 and 200 nm and did not differ practically from that of the support.

Apparatus and procedure. An all-glass flow apparatus working at atmospheric pressure has been used. This is depicted schematically in Fig. 1. Liquids were introduced into the reactor by means of mechanically operated syringes. Temperature in the reactor was maintained at 350 ± ± 0·5°C in all experiments, the catalyst sample weighed 0·5 to 1·5 g. The sample was taken from a stock which was sulphided and reduced in advance and was activated by heating in hydrogen gradually to 400°C. The initial activity of the catalyst in hydrodesulphurisation of thiophene decreased fastly by about 10% and then it remained constant; in the case of cyclohexene hydro-
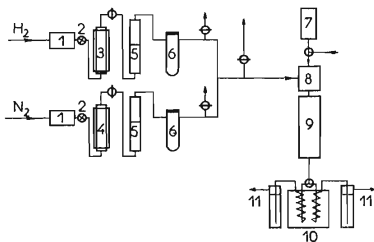

FIG. 1

Scheme of Apparatus

1 Manostats, 2 valves, 3 deoxygenation palladium catalyst, 4 nickel–manganese oxygen absorbant, 5 drying, columns 6 flow-meters, 7 feeder of liquids, 8 evaporator, 9 oven with reactor, 10 cooling traps, 11 H_2O absorbers.

genation, a similar fast activity decrease was considerable, by about 80%. At the same time, the sulphur content in catalysts decreased, too; Table I gives the sulphur content in sulphided catalysts and in catalysts exhibiting constant activity for hydrogenation of cyclohexene. Kinetic measurements were carried out in the region of steady activity which was satisfactorily constant. The catalysts were stored overnight in the reactor at room temperature in a stream of hydrogen. Of the reaction products, liquid substances were condensed at $-40°C$ and analysed by gas chromatography with the use of poly(ethylene glycol) on Cellite. In the case of cyclohexene hydrogenation these were cyclohexene, cyclohexane, methylcyclopentene and benzene; quantitative evaluation of chromatograms was based on calibration graphs which were linear for the region of the conversions used. In the case of thiophene desulphurisation the extent of the reaction was followed by iodometric titration of hydrogen sulphide trapped into ammonium solution of cadmium(II) chloride; the composition of C_4 hydrocarbons was not determined.

Kinetic data. Negligible influencing of kinetic data by external and internal diffusion was verified experimentally and by calculation. All experiments were carried out at atmospheric pressure, partial pressures of reactants were decreased by adding nitrogen. For both reactions, initial rates at different partial pressures of the organic compound and hydrogen were measured; initial reaction rates r_j^0 ($j = C$ for hydrogenation of cyclohexene and $j = T$ for hydrogenolysis of thiophene) were calculated as the ratios of the conversion x_j to the reciprocal space velocity W_i/F_j (for i-th catalyst). Conversions did not exceed 5 and 3% in the case of cyclohexene and thiophene, respectively; it was confirmed that these limits are reliably within the region of the linear dependence of x_j on W_i/F_j. This means that the reactor worked as pseudo-differential. In calculating r_C^0, the conversions attained were corrected for the amount of cyclohexane which could be formed by disproportionation of cyclohexene, and that with respect to the amount of benzene. This allowance was more important only in experiments with low partial hydrogen

TABLE I

Properties of Catalysts

Catalyst	Mol. ratio		Surface BET m^2/g	S content, %	
	Co/Mo	$\frac{(Co + Mo)}{Al_2O_3}$		after activation	after cyclohexene reaction
1	0·2	0·15	215	2·41	1·85
2	0·2	0·05	219	1·30	1·10
3	0·2	0·10	205	2·33	1·30
4	0·5	0·10	230	1·95	1·40
5	1·0	0·10	218	2·22	1·50
6[a]	0	0·10	188	—	—
7[b]		0·10	—	—	—
Alumina	—	—	230	—	—
Cherox					
36—00	0·47	0·15	160	2·40	0·55

[a] Without cobalt. [b] Without molybdenum.

pressure. The reproducibility of rate data was $\pm 15\%$. Each value of r_j^0 was calculated as an arithmetic mean of two x_j values.

Treatment of rate data. Sets of $r_C^0 - p_C^0 - p_H^0$ and $r_T^0 - p_T^0 - p_H^0$ dependences were treated by means of quasilinear regression[10] and suitable rate equations were selected from the set of 40 expressions of Langmuir–Hinshelwood type and from power equation. For discrimination between the models, the minimal sum of squared deviations between the calculated and experimental values of reaction rates Q_{min} was used. The selection was further restricted by excluding the equations which constants were negative. The best equations were then analysed by using Beale criterion[11] for 95% probability. In addition, the values of mean relative deviations between experimental and calculated reaction rates were calculated acrording to the expression:

$$\Delta = 100 \frac{Q_{min}^{0,5}}{\sum\limits^{n} (r_j^0)} . \qquad (1)$$

RESULTS AND DISCUSSION

Measurements with the catalysts summarised in Table I showed that hydrogenation and hydrogenolysis proceed on all the catalysts containing molybdenum. Catalyst 7 was inactive, in accordance with the literature. Isomerisation of cyclohexene to methylcyclopentene, which will be discussed in the subsequent work[9], was taking place on all catalysts $1 - 7$ and also on alumina.

Hydrogenation of cyclohexene over catalysts $1 - 6$ and also over industrial catalyst $36 - 00$ was best described by the equation

$$r_C^0 = k_C K_C p_C^0 (p_H^0)^2 / (1 + K_C p_C^0)^2 . \qquad (2)$$

Based on Beale criterion[11], the hydrogenation over catalysts 4 and 5 could be equally well described by the equation

$$r_C^0 = k_C K_C p_C^0 p_H^0 / [1 + \sqrt{(K_C p_C^0)}]^2 . \qquad (3)$$

Calculated values of constants k_C and K_C from Eq. (2) are summarised in Table II, along with the corresponding values of Q_{min} and Δ. The fit of Eq. (2) to experimental points is demonstrated in Fig. 2.

Hydrogenolysis of thiophene could be best described by the equation

$$r_T^0 = k_T p_T^0 p_H^0 / (1 + K_T p_T)^2 \qquad (4)$$

the constants of which are also in Table II and its course is depicted in Fig. 3.

With regard to the low sensitivity of the equations of Langmuir–Hinshelwood type to the value of constant K_j and with respect to the relatively large error with which this constant is usually determined, we have introduced the assumption

that their values for a given reaction are identical for all the catalysts. After putting the average values of K_C' and K_T' in Eqs (2) and (4), we calculated the values of rate constants $\bar{k}_C$ and $\bar{k}_T$ from experimental data. These values are also listed in Table II; it becomes evident that this procedure affected the values of the rate constants only within error limits. The validity of the assumption about K_C and K_T being the same for different catalysts and their scattering being given only by experimental error is indicated by a similarity of the curves for different catalysts in Figs 2 and 3. The position of the maximum, which — as can be easily proved for equations of Langmuir–Hinshelwood type — depends on the values of constants K_j (and on the total pressure of reactants) and is identical for all the catalysts.

TABLE II

Kinetic Parameters for Cyclohexene Hydrogenation (Eq. (2)) and Thiophene Hydrogenolysis (Eq. (4)) and Sorption Data for Oxygen on Cobalt–Molybdenum Catalysts

Quantity	Catalyst						
	1	2	3	4	5	6	Cherox 36—00
Hydrogenation of cyclohexene, 350°C							
$k_C \cdot 10^{-3}$	5·29	3·81	10·05	2·09	1·51	3·15	3·12
$K_C \cdot 10^{-2}$	1·03	0·92	2·13	1·11	0·64	1·62	0·76
Q_{min}	5·0	23·3	37·9	5·7	2·7	8·1	3·9
$\Delta, \%$	16	21	41	23	31	19	25
$k_C' \cdot 10^{-3}$ [a]	5·2	4·1	8·0	1·9	1·47	2·7	3·0
$k_{Cs}' \cdot 10^{-18}$	4·0	3·1	6·5	1·4	1·1	2·4	3·2
Hydrogenolysis of thiophene, 350°C							
$k_T \cdot 10^{-2}$	3·62	2·44	12·7	8·47	8·69	0·82	4·85
$K_T \cdot 10$	8·0	8·1	6·5	5·1	2·5	6·1	5·7
Q_{min}	5·0	7·9	238	148	57	2·9	10·5
$\Delta, \%$	24	26	15	26	15	19	9
$k_T' \cdot 10^{-2}$ [b]	3·7	2·4	12·8	7·8	5·8	0·92	4·8
$k_{Ts}' \cdot 10^{-17}$	2·9	1·8	10·4	5·7	4·5	0·8	5·0
Oxygen sorption, −78°C							
$L_O \cdot 10^{-16}$ [c]	9·0	8·3	11·4	8·0	7·5	7·5	—
$L_C \cdot 10^{-16}$	3·5	3·0	6·0	1·5	1·0	1·0	—

[a] For $K_C' = 102$ MPa^{-1}, [b] for $K_T' = 69$ MPa^{-1}, [c] calculated on the basis of the measurement with the reduced sample of pure MoO_3 having a surface of 0·5 m^2 g^{-1}; the oxygen consumption corresponded to $L_O = 61·7 \cdot 10^{16}$ sites per m^2.

For cyclohexene hydrogenation this maximum lies close to the molar fraction $N_C \approx 0.1$, for thiophene hydrogenolysis it is near to $N_T \approx 0.15$.

The procedure used for concentration of all the differences in the activity of catalysts in one quantity for each model reaction, k_C' and k_T', has the advantage for further interpretation, *i.e.* it avoids the problems of the relation between the reaction mechanism and the rate equation. For heterogeneous catalysed reaction this relation is not simple. With regard to necessary approximations and a relatively large experimental error, it is not possible to deduce mechanistic conclusions from the form of equations[12]. Relationships between the activity of the catalysts for hydrogenation and hydrogenolysis can be therefore discussed only on the basis of determined series of rate constants k_C' and k_T', the values of which are proportional to the
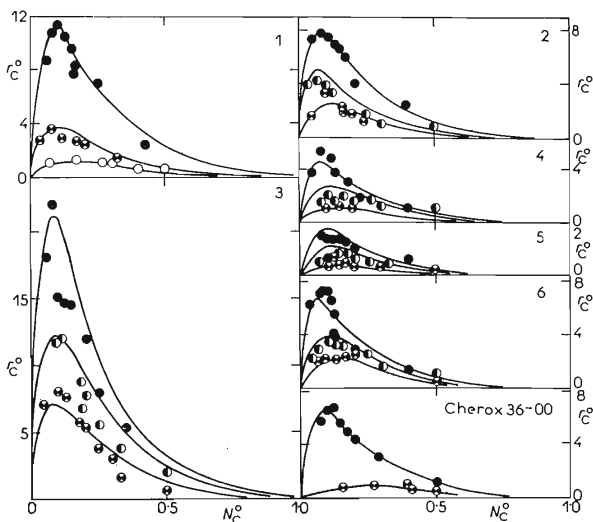

FIG. 2

Dependence of r_C^0 on the Composition of the Feed for Different Catalysts

Points are experimental, curves are calculated by Eq. (2). Total pressure of reactants (the residue to the pressure 0·1 MPa is nitrogen) $p_C^0 + p_H^0 =$ ● 0·1 MPa, ◐ 0·08 MPa, ◓ 0·06 MPa, ○ 0·03 MPa.

heights of maxima in Figs 2 and 3 or on the basis of specific rate constants k'_{Cs} and k'_{Ts} which are related to the unit surface of the catalyst (BET).

From Table II it is evident that the highest activity for both reactions is exhibited by catalyst 3, whose molar composition from Table I gives after recalculation to usual
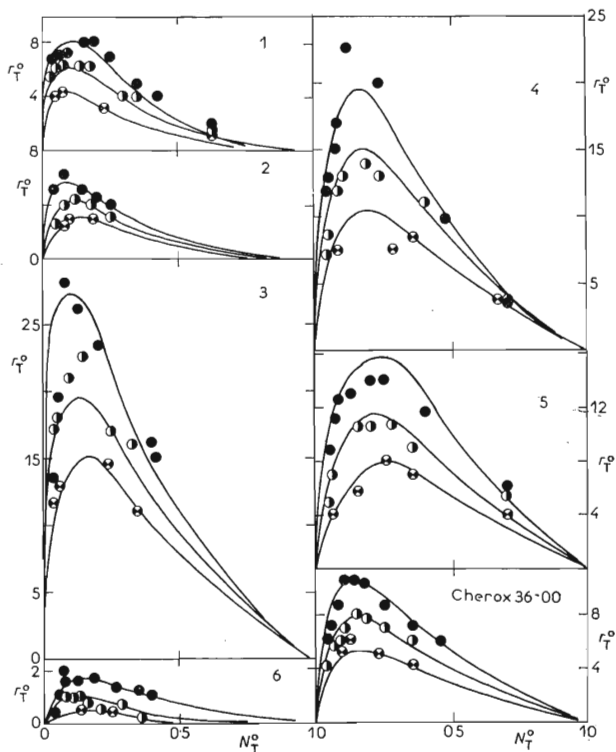

Fig. 3

Dependences of r_T^0 on the Composition of the Feed for Different Catalysts

Points are experimental, curves are calculated by Eq. (4). The designation of points as in Fig. 2.

mass portions 10·4%, MoO_3 and 1·2% Co_2O_3 content in nonactivated sample. The maximum of the activity is very pronounced especially for hydrogenation. Further inspection of the data in Table II shows that the activity depends both on the Co/Mo ratio and on the total content of active components which is expressed by the ratio $(Co + Mo)/Al_2O_3$. In Fig. 4 are plotted hydrogenation rate constants against hydrogenolysis rate constants. It holds for both the series with a constant Co/Mo ratio and the series with a constant $(Co + Mo)/Al_2O_3$ ratio that the higher the activity for the hydrogenation, the higher the activity for the hydrogenolysis. The curves in Fig. 4 are not meant to express a correlation but are intended to designate only the points which are kindred. The catalyst without cobalt and the industrial catalyst which was prepared by another procedure does not fit these series.

Recently, a method for determining surface concentration of molybdenum in non-sulphided catalysts used in this work was developed in this laboratory, based on irreversible adsorption of oxygen at $-78°C$ on reduced samples[8]. It was of interest to compare specific rate constants for hydrogenation and hydrogenolysis with the specific value of oxygen adsorption L_s. The corresponding data are given in Table II and show parallel trends. Fig. 5a demonstrates that L_s correlates well with the rate constant for hydrogenation of cyclohexene, k'_{Cs}; a small deviation is observed only for catalyst 6 which does not contain cobalt. On the other hand, a similar dependence for thiophene hydrogenolysis splits into two curves (Fig. 5b), one for catalysts 2, 1 and 3 and the other for catalysts 5, 4 and 3, *i.e.* in dependence upon which of the parameters (Co/Mo ratio or $(Co + Mo)/Al_2O_3$ ratio) changes along the series.

For that reason the dependence in Fig. 5a for hydrogenation activity is more suitable for analysis. At the same time, we can disregard the fact that the adsorption
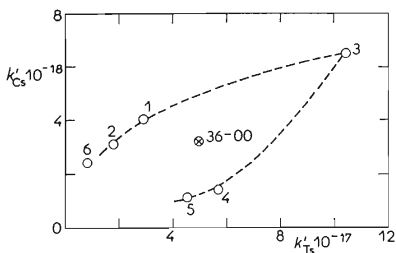

FIG. 4

Specific Rate Constants for Hydrogenation of Cyclohexene and for Hydrogenolysis of Thiophene over Different Catalysts

of oxygen was measured on nonsulphided reduced catalysts and the hydrogenation of cyclohexene on the sulphided and reduced catalysts; the literature[13] shows that the activation of the catalyst involves reduction and not sulphidation. The linear dependence in Fig. 5a can be interpreted with the use of the assumption that the experimental rate constants $(k'_{C_s}, k'_C$ and $k_C)$ are the product of the rate constant on one site k^0_C and the concentration of active sites, *e.g.*

$$k'_{C_s} = k^0_C L_C , \qquad (5)$$

where L_C is the number of active sites per unit area of the surface. As follows from Fig. 5a, k^0_C is identical for all the catalysts which differ only in the L_C values. Extrapolation of the straight line in Fig. 5a to the value of k'_{C_s} equaling to zero provides the estimation of the number of inactive molybdenum atoms on unit surface L_n. Provided that chemisorption of oxygen on molybdenum atoms has the stoichiometry 1 O per 1 Mo and also that the adsorption of cyclohexene is of the simple stoichiometry 1 C_6H_{10} per 1 Mo, we can write for the straight line in Fig. 5a

$$L_O = L_n + mk'_{C_s} \qquad (6)$$

and with regard to Eq. (5) also $L_C = L_O - L_n$ and $m = 1/k^0_C$. The L_C values for different catalysts were read from Fig. 5a and are presented in Table II.

From the common value of k^0_C estimated from the slope of the straight line in Fig. 5a as being equal to $1 . 10^2 \, s^{-1} \, MPa^{-1}$ one can calculate the turn-over number for partial pressures $p^0_C = 0.01$ MPa and $p^0_H = 0.09$ MPa, for which the initial
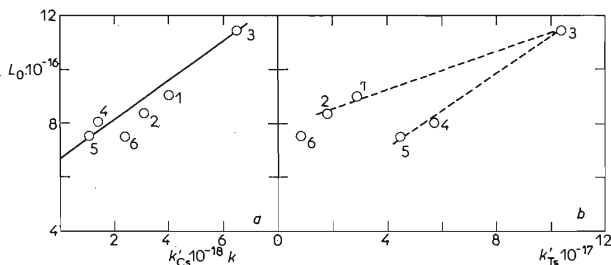

FIG. 5

Relationships between Oxygen Chemisorption and Specific Rate Constants for Cyclohexene Hydrogenation and Thiophene Hydrogenolysis

reaction rate of cyclohexene hydrogenation r_C^0 attained maximum in our experiments (compare Fig. 2). This value equals approximately to $0.2 \, s^{-1}$. A similar estimation for thiophene hydrogenolysis, based on limit possibilities according to Fig. 5b, yields turn-over numbers within 0.35 to $0.70 \, s^{-1}$ range. Although changed assumptions about the stoichiometry of oxygen chemisorption and of cyclohexene adsorption give other turn-over numbers, these are, however, comparable within one order of magnitude.

Discussed estimates of the number of active sites from oxygen chemisorption and kinetics are in accordance with physical possibilities. For the ideal (100) surfaces of MoO_3 (rhomb.) or MoO_2 (tetr.), the surface molybdenum atom concentrations correspond to approx. 10^{18} per m^2. The titration of the reduced sample of pure MoO_3 by oxygen gave a value of about 10^{17} atoms per m^2 (both for the stoichiometry $1 \, O : 1 \, Mo$ and for $1 \, O_2 : 1 \, Mo$) and for our supported catalysts the value by one order of magnitude smaller. This sequence is in accord with expectation. The inactive portion L_n for cyclohexene hydrogenation amounts to 50 up to 80%, as estimated from Fig. 5a. In the case of thiophene hydrogenolysis, similar relationships hold obviously for catalysts 3, 4 and 5. For the less active catalysts this portion is markedly greater.

Although having many features in common, the behaviour of catalysts in respect to cyclohexene and thiophene differs in some important points. This was indicated already by Fig. 4. Fig. 5 showed that the reason for the deviations from parallel behaviour of the series of our catalysts toward cyclohexene and thiophene is the more complicated dependence of the hydrogenolytic activity of catalysts on their composition. Notwithstanding, the similar shape of the kinetic curves in Fig. 3 speaks for the same type of active sites on all the catalysts, inclusive the industrial $36-00$ catalyst which was prepared by a different procedure. The reason for the more complicated relationships between the surface concentration of molybdenum atoms for oxygen chemisorption and the activity for hydrogenolytic cleavage of thiophene may be greater steric demands for the addition of hydrogen to the aromatic molecule of thiophene (compared to the addition to the double bond of cyclohexene) or the multistep mechanism of the reaction of thiophene with hydrogen to form hydrogen sulphide and C_4 hydrocarbons which involves tetrahydrothiophene as an unstable intermediate product[7].

In spite of this uncertainty, one can conclude that our kinetic study of the relationships between the composition and activity of the cobalt–molybdenum catalysts provided a relatively simple picture, which with the use of and in agreement with the earlier knowledge[1−3], can be summarised as follows. The active sites of the catalyst surface, which are formed by atoms of molybdenum in lower valence state, are of the same nature for catalysts of different composition. Cobalt, which is structural promotor, increases the concentration of these sites when used in smaller

amounts. After exceeding the optimum Co/Mo ratio, which depends on the procedure used for preparing the catalyst, the activity again decreases. The concentration of active sites is affected also by the ratio of the active components to the support, $(Co + Mo)/Al_2O_3$, and that in a more complex way in the case of thiophene reaction than in the case of cyclohexene hydrogenation.

LIST OF SYMBOLS

F_j feeding rate of compound j (mol h^{-1})

k_C rate constant of cyclohexene reaction   (mol h^{-1} kg$_{cat}^{-1}$ MPa^{-2})

k_C' corrected rate constant of cyclohexene reaction   (mol h^{-1} kg$_{cat}^{-1}$ MPa^{-2})

k_{Cs}' specific rate constant of cyclohexene reaction   (molecules s^{-1} m^{-2} MPa^{-2})

k_C^0 rate constant of cyclohexene reaction on one site   (s^{-1} MPa^{-2})

k_T rate constant of thiophene reaction   (mol h^{-1} kg$_{cat}^{-1}$ MPa^{-1})

k_T' corrected rate constant of thiophene reaction   (mol h^{-1} kg$_{cat}^{-1}$ MPa^{-1})

k_{Ts}' specific rate constant of thiophene reaction   (molecules s^{-1} m^{-2} MPa^{-1})

L_C concentration of active sites for cyclohexene reaction   (site per m^{-2})

L_n concentration of inactive sites   (site per m^{-2})

L_O concentration of Mo atoms absorbing oxygen   (site per m^{-2})

m slope of the dependence in Fig. 5a (Eq. (6))

n number of experimental points

$N_j^0 = F_j/(F_j + F_H)$

p_j^0 partial pressure of compound j in the feed   (MPa)

r_j^0 initial reaction rate of compound j (mol h^{-1} kg$_{cat}^{-1}$)

Q_{min} minimal sum of squared deviations of reaction rates r_j^0 (mol^2 h^{-2} kg$_{cat}^{-2}$)

W_i mass of catalyst i (kg)

x_C conversion of cyclohexene to cyclohexane   (—)

x_T conversion of thiophene to hydrogen sulphide   (—)

Indices

C   cyclohexene

H   hydrogen

i catalyst

j cyclohexene or thiophene

n   inactive

O   oxygen

s   specific

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