HYDROGENATION OF ALKENES
ON A NICKEL–TUNGSTEN–ALUMINA CATALYST

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Eleven C_2 to C_8 alkenes were hydrogenated on a reduced sulphided industrial nickel–tungsten catalyst. Kinetics of the reaction was investigated in detail for ethylene and data were correlated by different equations. Best fit was obtained by three equations of the Langmuir–Hinshelwood type and these were used to describe hydrogenation of the other alkenes. Logarithms of the rate constants obtained were correlated linearly with the sum of steric constants E_0^s of substituents of semihydrogenated state $R^1R^2R^3C$-*. Also adsorption coefficients of alkenes were structure dependent, increased with molecular weight of alkene and correlated roughly with boiling points.

In previous communication[1] we reported on structure effects of alkenes on the rate of their hydrogenation on an industrial $CoO-MoO_x-Al_2O_3$ catalyst. On the basis of the effects and their quantitative correlation by a linear free energy relationship we concluded that the rate determining step of the successive addition of two hydrogen atoms across the $C=C$ double bond is the second step, *i.e.* the transformation of adsorbed semihydrogenated state to alkane. This finding demonstrates significant differences from hydrogenation on metals where the slower step is the first one, *i.e.* the formation of semihydrogenated state. As found by LFER correlations, in both cases the hydrogenation rate is controlled by steric hindrance, *i.e.* for metals by the substituents on the double bond of $R^1R^2C=CR^3R^4$ (for review see ref.[2]) and for our catalyst, the active centers of which are formed by low coordinated surface molybdenum atoms $(cf.^3$ and references therein), by groups R in the surface compound $R^1R^2R^3$-*.

The aim of the present work was to verify whether the mechanism found for the molybdenum catalyst is valid also for other nonmetallic hydrogenation catalysts. For this purpose, we used different type of industrial hydrorefining catalyst, *i.e.* a sulphided nickel–tungsten on alumina catalyst. The method used was the same as in our previous work[1].

EXPERIMENTAL

Catalyst was industrial Cherox 34-02 (Chemické závody, Litvínov) containing 3·5% NiO and 27% WO_3, the rest being alumina. Pellets were disintegrated and the 0·16—0·40 mm fraction

was used in experiments. The catalyst was reduced and sulphided in a stream of hydrogen and hydrogen sulphide (10 : 1) for 4 h. Before each experiment, the catalyst was re-reduced by hydrogen at 500°C for 3 h. The catalyst activity was well reproducible.

Alkenes were of the same origin and purity as in the previous work[1]. Also a flow apparatus, procedure and analysis of products were described in the mentioned communication. Reaction temperature was 300°C and the conversion of alkenes did not exceed 8 per cent.

Kinetic measurements with ethylene involved determination of initial reaction rates r_0 for different ratios of partial pressures of ethylene and hydrogen in the feed, total pressure of these components was changed by addition of nitrogen. Each r_0 value is an average of 2—4 measurements. Hydrogenation rates of the other alkenes were determined only at the total pressure equaling to atmospheric, *i.e.* without diluting the reaction mixture with nitrogen.

Kinetic data for ethylene hydrogenation were treated by different equations of the Langmuir–Hinshelwood type and by power equation. Data were correlated by these equations in linearized form, first by means of the quasilinear regression[3,4]. This led to selection of nine expressions which best fit the data. These were then verified by nonlinear regression using the Marquardt procedure, the values of constants obtained by quasilinear regression being used as initial estimates.

RESULTS AND DISCUSSION

Basic kinetic behaviour of the studied system alkene–hydrogen on the sulphided nickel–tungsten catalyst was examined with ethylene at 300°C. Obtained dependences of initial hydrogenation rates on the composition of reaction mixture are shown in Fig. 1. The data were treated by the method described in Experimental. Best equations found, both by quasilinear and by nonlinear regression, were the following three relations

$$r_0 = kK_AK_Hp_Ap_H/(1 + K_Ap_A + K_Hp_H)^2 , \qquad (1)$$

FIG. 1

Dependence of initial reaction rates r_0 (mol h^{-1} kg$_{cat}^{-1}$) of ethylene hydrogenation on sulphided nickel–tungsten catalyst at 300°C on mole fraction of ethylene in mixture with hydrogen in the feed $y_A = p_A/(p_A + p_B)$. Points are experimental, curves were calculated according to Eq. (1) for $k = 2\,023$ mol h^{-1} kg$_{cat}^{-1}$, $K_A = 19\cdot2$ MPA^{-1}, $K_H = 6\cdot05$ MPa^{-1}. Total pressure $p_A + p_B$ for individual curves 1a 0·1 MPa, 1b 0·07 MPa, 1c 0·05 MPa, 1d 0·03 MPa
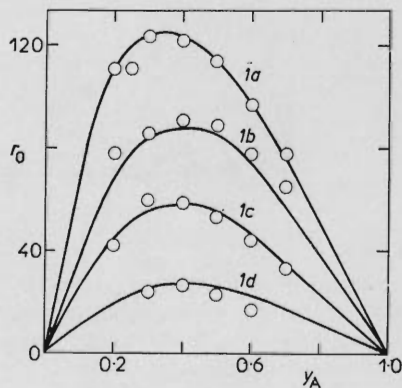
$$r_0 = kK_AK_Hp_Ap_H/(1 + K_Ap_A + K_Hp_H)^3 \,, \tag{2}$$

$$r_0 = kK_AK_Hp_Ap_H/[1 + K_Ap_A + (K_Hp_H)^{0.5}]^3 \,, \tag{3}$$

where k is the rate constant, K_A and K_H are adsorption coefficients of alkene and hydrogen, p_A and p_H are partial pressures of alkene and hydrogen in the feed. The sum of squared deviations equaled to 515 for Eq. (1), 477 for Eq. (2) and to 606 mol^2 . . h^{-2} kg$_{cat}^{-2}$ for Eq. (3). Eq. (1) was found also by Vyskočil and Kraus[3] as the best expression for the rate of hydrogenation of cyclohexene on cobalt–molybdenum catalysts and this equation was taken as the basis for calculating rate constants for different alkenes in our previous work[1].

Measurements of the rates of hydrogenation of other ten alkenes gave dependences which are shown in Fig. 2. It is evident that the position of maximum with respect to the coordinate of mole fraction y_A shifts with increasing molecular weight of alkene to left hand side. As in equations of the Langmuir–Hinshelwood type the position of this maximum relates to the ratio of values of adsorption coefficients K_A and K_H and since one can assume that the value of the adsorption coefficient of hydrogen K_H is constant, this means that the adsorptivity of alkene increases with molecular weight, in contradistinction to the cobalt–molybdenum catalyst for which the position of maximum is the same for all alkenes[1]. The height of maximum is directly
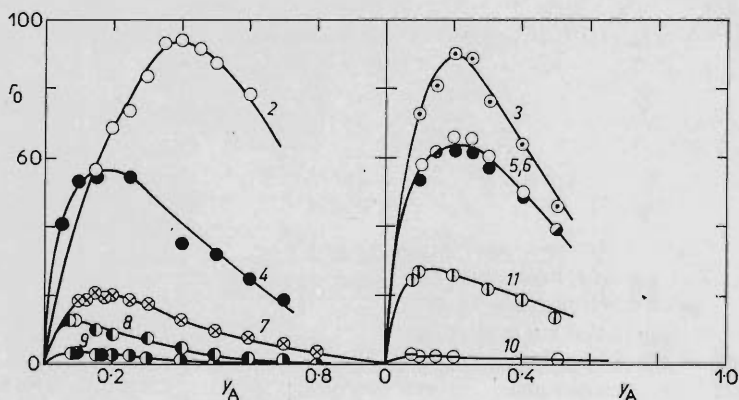

FIG. 2

Dependences of initial reaction rates r_0 (mol h^{-1} kg$_{cat}^{-1}$) of hydrogenation of alkenes on sulphided nickel–tungsten catalyst at 300°C on mole fraction of alkene in mixture with hydrogen y_A under atmospheric pressure (0·1 MPa). *2* Propene, *3* 1-butene, *4* isobutene, *5* cis- and trans-2-butene, *7* 1-hexene, *8* 2,3-dimethyl-1-butene, *9* 3,3-dimethyl-1-butene, *10* 2,3-dimethyl-2-butene, *11* 1-octene

proportional to the rate constant and changes with the structure of alkenes within two orders of magnitude, similarly as in the case of the cobalt–molybdenum catalyst[1].

Kinetic data for the C_3—C_8 alkenes were obtained only for one total pressure $p_A + p_H$ and therefore only two constants of the rate equation could be reliably determined. We presumed that the value of the adsorption coefficient K_H remains identical in all cases. Hence, in treatment of data by Eqs $(1)-(3)$, K_H value used was that obtained from the data for ethylene. By this way, we calculated k and K_A values for 10 alkenes shown in Fig. 2; these are presented in Table I. The dependences of rate constants on alkene structure have the same trend, regardless of the expression which was used for their calculation. Sequence of relative reactivities is analogous

TABLE I

Values of constants of equations $(1)-(3)$ for different alkenes and of constants of correlations (4) and (5) for corresponding series of rate constants and adsorption coefficients

No	Alkene	Eq. (1)		Eq. (2)		Eq. (3)	
		k^a	$K_A{}^b$	k^a	$K_A{}^b$	k^a	$K_A{}^b$
1	Ethylene^c	2 020	19	6 420	10·0	11 940	11·1
2	Propene	1 750	12	5 420	6·7	10 580	6·9
3	1-Butene	1 060	61	3 570	27	6 470	30
4	Isobutene	702	75	2 400	32	4 330	34
5	cis-2-Butene	813	58	2 730	26	4 960	28
6	trans-2-Butene	778	56	2 610	25	4 740	27
7	1-Hexene	237	80	805	33	1 450	36
8	2,3-Dimethyl- -1-butene	33·2	118	113	45	202	49
9	3,3-Dimethyl- -1-butene	143	224	468	70	832	77
10	2,3-Dimethyl- -2-butene	28·9	194	96·3	68	171	74
11	1-Octene	328	88	1 130	36	2 020	40
Eq. (4) a		2·91	—	3·42	—	3·69	—
b		0·58	—	0·63	—	0·58	—
r_k		0·95^d	—	0·98^d	—	0·96^d	—
Eq. (5) c		—	2·02	—	1·75	—	1·80
d		—	−0·33	—	−0·36	—	−0·37
r_k		—	0·79^d	—	—	0·84^d	0·84^d

^{a} mol h^{-1} kg$_{cat}^{-1}$, ^{b} MPa^{-1}, ^{c} K_H values for Eq. (1) 6·05, Eq. (2) 3·29, Eq. (3) 2·34, ^{d} critical r_k for 99% level of significance 0·73, for 99·9% level of significance 0·85.

to that for the hydrogenation on the cobalt–molybdenum catalyst; the only exception is 3,3-dimethyl-1-butene. For purposes of interpretation it is important that the constants for *cis-* and *trans-*2-butenes and for isobutene are very close to each other and the same goes also for the pair 2,2-dimethyl-1-butene and 2,3-dimethyl-2-butene. In previous work[1], this agreement was assumed to prove that species of the same structure react in the rate determining step, which can be the semihydrogenated state. The same assumption is justified also for the reaction on the nickel–tungsten catalyst. Similarly as earlier[1], we correlated rate constants by the relation (4) where E_s^0 constants are Palm steric constants, *i.e.* Taft steric E_s

$$\log k = a + b \sum E_s^0 , \qquad (4)$$

constants corrected for hyperconjugation contribution. Their sum was calculated for the substituents of the semihydrogenated state $R^1 R^2 R^3 C\text{-}*$. Values of the coefficients a and b and of the correlation coefficient r_k are presented in Table I and an example in which we used k values from Eq. (2) is shown in Fig. 3. On the basis of this correlation one can conclude that also in the case of the nickel–tungsten catalyst the reaction is controlled by transformation of the semihydrogenated state to alkane, similarly as for the cobalt–molybdenum catalyst[1].

Rate constants obtained from all three equations gave good and nearly identical correlations with structure effects (Table I). However, it is pertinent to stress that
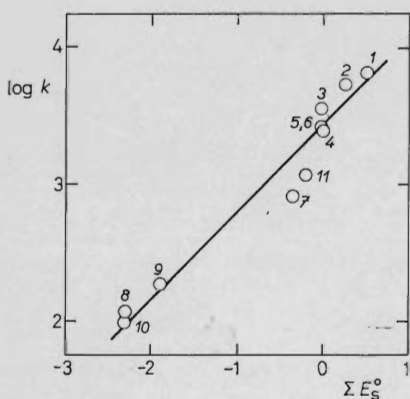

FIG. 3

Correlation of rate constants calculated from Eq. (2) against the sum of steric constants of substituents of semihydrogenated state $R^1 R^2 R^3 C\text{-}*$ (Eq. (4))
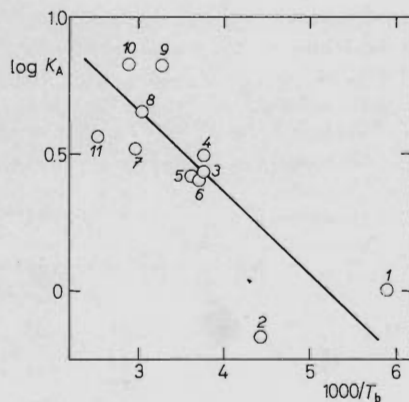
FIG. 4

Correlation of adsorption constants calculated from Eq. (2) against reciprocal values of boiling point T_b (K) of alkene (Eq. (5))

Eqs (1)−(3) differ little one from another and their fit to experimental data is practically identical. This confirms our earlier and repeated experience that for a successful LFER correlation the form of the rate equation used to calculate the constants is not decisive but that the least as possible deviations of experimental from calculated kinetic dependences play prevailing role.

Qualitative analysis of dependences in Figs 1 and 2 shows that maxima on the curve tend to shift to left hand side with increasing molecular weight of alkene. This manifests itself also in the calculated adsorption coefficients of alkenes K_A, presented in Table I. This fact could be caused by several reasons; one of them could be an increase in the inductive effect of alkyl substituents with their increasing size, leading to the change of electron density on the double bond. Steric effect of substituents increases similarly. However, as the adsorption coefficients increase with increasing size of the molecule, we should deal here with the steric enhancement of adsorption, which does not seem likely. Another probable interpretation is the increase in adsorptivity due to the lower volatility of alkenes. These hypotheses was tested by means of different linear correlations, i.e. $\log K_A$ with the sum of Taft induction constants σ and E_s (or E_s^0) of substituents on the double bond. The best, although not fully satisfactory, correlation was obtained with $\log K_A$ against reciprocal boiling point T_b, the boiling point being used as a measure of the volatility of substances (Eq. (5)).

$$\log K_A = c + 1000d/T_b \qquad (5)$$

Fig. 4 shows a certain scattering of data; this is indicated also by the correlation coefficients (Table I). We believe that this scatter is caused mainly by experimental error and by uncertainty in calculation of the value of adsorption coefficients of Langmuir–Hinshelwood equations, the error being — according to out experience — in best cases $\pm 20\%$ but often even $\pm 100\%$. One cannot exclude, however, that this scatter disguises the effect of structure which is less pronounced compared to the effect of the mass of the alkene molecule.

As far as classical concepts about mechanism of heterogeneous catalytic reactions are concerned, studied hydrogenation on nickel–tungsten catalyst exhibits "normal" behaviour, i.e. both constants of the rate equation which relates to reacting alkene depend on its structure. This is a difference from the analogous system with the cobalt––molybdenum catalyst for which only the rate constant was structure dependent and the adsorption coefficient did not change for the whole series of alkenes. This fact arises a question whether simple physical interpretation of the so called adsorption coefficients from rate equations is correct and whether they are not the products or sums of rate and equilibrium constants of separate steps of complex reaction mechanism, in which there is possibility of compensation of effects (see discussion of physical meaning of these constants in previous work[1]).

REFERENCES

1. Uchytil J., Jakubíčková E., Kraus M.: J. Catal. *64*, 143 (1980).
2. Kraus M.: Advan. Catal. Relat. Subj. *29*, 151 (1979).
3. Vyskočil V., Kraus M.: This Journal *44*, 3676 (1979).
4. Kubíček M., Marek M., Eckert E.: Technometrics *13*, 601 (1971).

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