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The Mechanism of Catalytic Hydrogenolysis of Ethane Over Nickel

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Hydrogenolysis of ethane was investigated on nickel powder catalyst from 170 to 320°C. The reaction was first order with respect to ethane and it was inhibited by hydrogen at sufficiently low temperature whereas at high temperature it was independent of hydrogen pressure. This behaviour as well as the relation among the energies of activation of ethane exchange, methane exchange and ethane hydrogenolysis (20, 30 and 39 kcal $mole^{-1}$, respectively) give further evidence for the validity of the kinetic picture described by Sinfelt and Taylor.

The application of deuterium and tritium in place of hydrogen offers new information for the mechanism of hydrogenolysis. The distribution of deuterated methane shows that the initial step for ethane exchange and hydrogenolysis is probably common and the adsorption with C–C bond rupture may be ruled out. In comparison with methane–deuterium exchange under the same condition, clear evidence was obtained that methane desorption is fast and may not be a rate-limiting step. For this direct proof has not been found in literature.

An explanation is given for the change in distribution of deuterated methane formed in the hydrogenolysis taking place with variation of temperature and activity of catalyst.

INTRODUCTION

The catalytic hydrogenolysis of aliphatic hydrocarbons is one of the basic reactions by which the reforming process in petroleum industries is accompanied. Because of the importance of this reaction it has been studied by numerous authors. Most studies have been focused on the behavior of ethane in hydrocracking over different transition metals on supports (*1–7*). From these results it was postulated that the reaction begins with the dissociation of hydrogen atoms from ethane molecules forming unsaturated surface radicals. The reaction of these surface radicals with hydrogen leads to the cleavage of C–C bond and it is followed by the desorption of methane. This latter step is held to be fast and therefore it is generally accepted that in ethane hydrogenolysis the C–C rupture is the rate-limiting step.

However, Anderson and Baker (*8*) studying the hydrocracking of saturated hydrocarbons argued against the mechanism described above. According to their result based on the adsorption measurement of hydrocarbons, the initial adsorption of ethane on Ni films led to C–C rupture and so to the formation of monocarbon fragments. The rate-determining step is assumed to be the desorption of these radicals from the catalyst surface. This is supported partly by the recent data of propane hydrogenolysis carried out by Shephard (*9*). This statement resulted from the agreement between the experimental and calculated change of methane formation as a function of temperature.

This idea was supported also by Galwey (*10*) who studied the cracking of different hydrocarbons on nickel carbide..

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All these works, however, cannot definitely decide on which process, viz. C–C rupture on the catalyst or desorption of the reaction products from the surface, is the rate-determining step.

The object of this work has been to obtain more information about the precise mechanism of the hydrogenolysis of ethane on metal catalysts. Hydrogen isotopes (deuterium and tritium) have been used to study the exchange process during the hydrogenolysis.

Experimental Methods

Nickel powder catalyst was prepared from $Ni(OH)_2$ by reduction with hydrogen at 360°C for 1 hr after which the catalyst was evacuated at the same temperature for 1 hr.

Ethane was taken from a cylinder and was distilled three times under vacuo at liquid nitrogen temperature. Tritium-labelled hydrogen as well as carrier free deuterium gas was prepared by the reaction of sodium with water and was purified by passing through a heated palladium thimble.

The reaction was carried out in a glass circulating apparatus (*11*). Ethane and hydrogen were premixed before admitting to the catalyst. In the case of deuterium the analysis was carried out with an AEI MS 10 mass spectrometer. The reaction mixture leaked through a fine capillary tube into the mass spectrometer and methane and ethane were determined together at given time intervals. Twelve eV was applied and at this electron energy the fragmentation of methane was negligible. In the case of ethane a correction was applied for the naturally occuring carbon-13 and for the fragmentation resulting from the loss of one and two hydrogen atoms. All these procedures were carried out as in the case of methane exchange studied by Kemball (*12*). A calibration was used at different over-all pressures and compositions to obtain the true value for the quantities of methane and ethane. In this way the relative amounts of different deuterated species in ethane and methane could be determined.

A radiogaschromatograph was applied to measure the extent of hydrogenolysis and that of exchange in the case of tritium labelled hydrogen. The method has been described earlier (*11*). By using this method the quantity and radioactivity of hydrogen, methane and ethane could be simultaneously measured. From these data the specific radioactivity of all substances could be calculated. The evaluation of the gaschromatographic data shows that the carbon balance in the gas phase is correct within the experimental error.

All the raw data were corrected for isotope and fragmentation correction by using an ICT 1900 computer. The data concerning the power of the reaction were also evaluated by the method of multiple regression (*13*) using the same computer.

Reproducibility lay within about 3–4%, apart from the first few experiments on fresh catalyst the activity of which was successively lost until a constant level was achieved.

Results

The only product of the ethane hydrogenolysis was methane and its formation was followed at different temperature and partial pressures of ethane and hydrogen. Two methods were used to measure the order of reaction. Either the pressure of one component was kept constant and the effect of the other examined, or the pressures of both substances were changed together. In both cases the initial slopes of the curves plotted as the pressure of methane formed versus time were applied for the calculation of the order of reaction. In Table 1 the result of this measurement is summarized between 174–323°C.

It seems that the order of hydrogenolysis with respect to ethane is positive and there is a slight decrease as the temperature increases. The effect of hydrogen is opposite to that of ethane. At higher temperature the formation of methane is independent of the hydrogen pressure but at relatively low temperature it inhibits the reaction. This behaviour of hydrogen is very similar to that found by Sinfelt and

TABLE 1

$w = k \cdot p^{a}_{C_2H_6} \cdot p^{b}_{H_2}$

THE CHANGE OF THE ORDER OF HYDROGENOLYSIS WITH TEMPERATURE

°C	$p_{C_2H_6}$ Torr	p_{H_2} Torr	a	b
278	23–78	22–85	1.0	0.0
310	25–80	25–130	0.85	0.0
323	25–86	40–130	0.78	0.0
262.5[a]	7.9	8.4–31.5	—	0
174[a]	7.9	8.4–31.5	—	−1.4
250[a]	6.8–34	34–61.2	0.9	−0.7

[a] Using D_2 gas.

Taylor (*14*) in the ethane hydrogenolysis on cobalt-on-silica catalyst.

Methane was considered not to exert an influence on the hydrogenolysis. To prove this assumption methane was added to the initial mixture of hydrogen and ethane in different quantities and the hydrogenolysis was investigated at different temperatures. The initial rate of methane formation from 183–240°C remained the same showing that the coverage of radicals resulting from methane adsorption is negligible compared to those from ethane and hydrogen. In Fig. 1 typical runs are presented with and without added methane.

The energy of activation calculated from the straight lines in Fig. 2 is 37–40 kcal mole^{-1}. The difference in the absolute value of log w^0 by using tritium and deuterium is due rather to the different activity level of the catalysts than the application of hydrogen isotopes. This statement is based on the experimental finding that there is no difference in the ethane exchange using different hydrogen isotopes (*22*).

The usefulness of the application of hydrogen isotopes in the hydrogenolysis is to find the correlation, if any, between hydrogen exchange (*15*) and the hydrogenolysis of ethane. A typical set of data are presented in Fig. 3 showing the change of specific radioactivity of ethane, methane and hydrogen by using tritium labelled hydrogen. It seems interesting that the specific radioactivity of methane is much higher than that of hydrogen and ethane.

The data resulting from the application of deuterium gas in studying the ethane hydrogenolysis are summarized in Table 2.

In the first three columns the temperature of reaction and the partial pressures

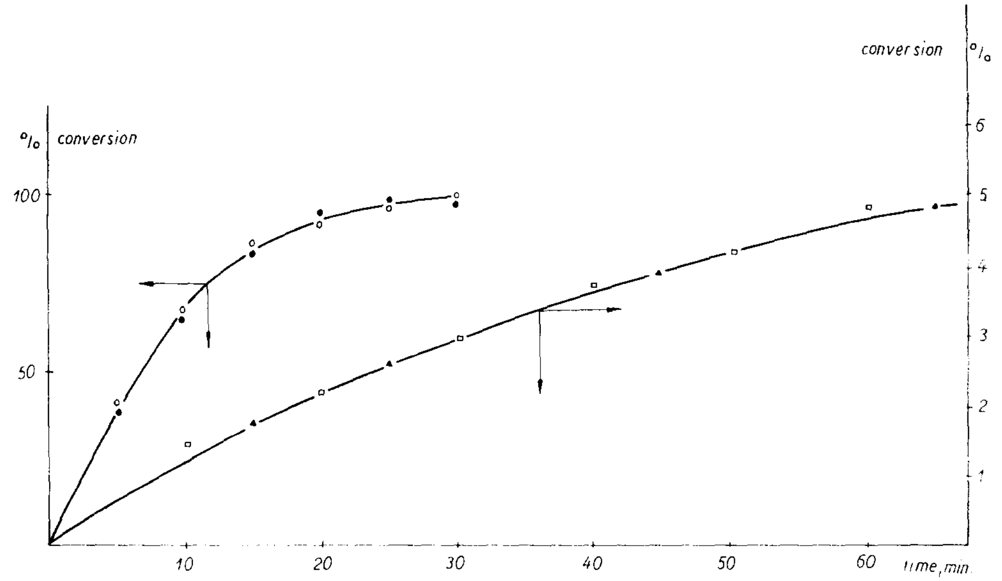

FIG. 1. Percentage conversion of methane formation with and without added methane as a function of time. ○: $p_{C_2H_6}$ = 3.94 Torr, p_{D_2} = 11.83 Torr; ●: $p_{C_2H_6}$ = 3.06 Torr, p_{CH} = 1.97 Torr, p_{D_2} = 10.74 Torr; T = 240°C. □: $p_{C_2H_6}$ = 6.82 Torr, p_{D_2} = 14.47 Torr; ▲: $p_{C_2H_6}$ = 6.82 Torr, p_{CH_4} = 1.97 Torr, p_{D_2} = 14.47 Torr; T = 182°C.

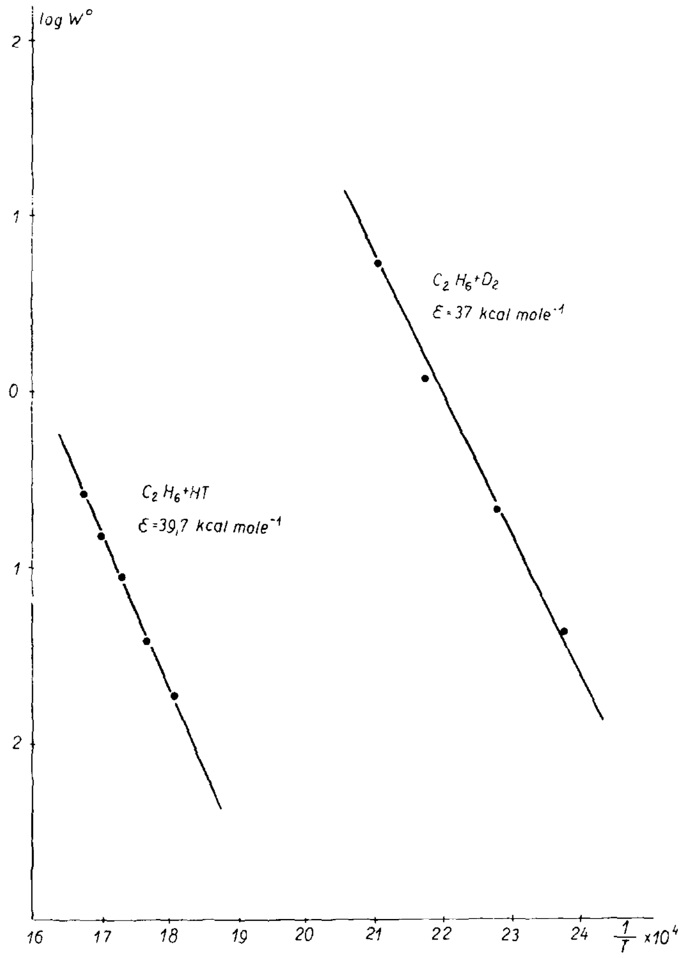

FIG. 2. The plot of log W^0 as a function of $1/T$.

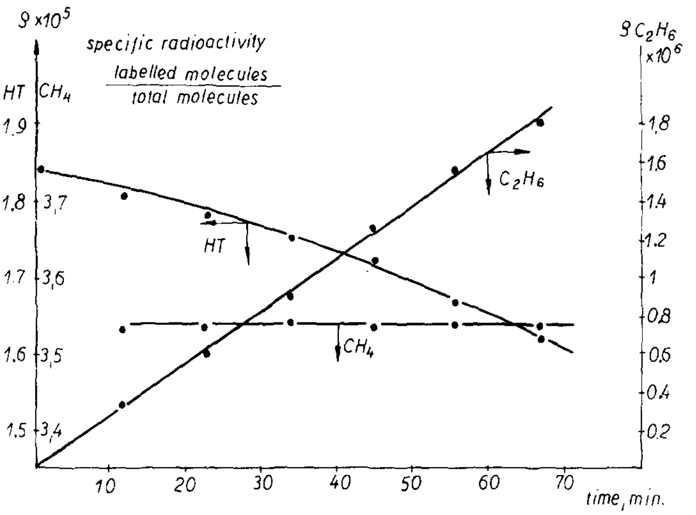

FIG. 3. The change of specific radioactivity of ethane, methane and tritium labelled hydrogen during the hydrogenolysis; T = 325°C.

TABLE 2

°C	pTorr		$\frac{p_{D_2}}{p_{C_2H_6}}$	$W^0_{\text{EXCH.}}$ % min^{-1}	$W^0_{CH_4}$ % min^{-1}	$\frac{W^0_{\text{EXH}}}{W^0_{CH_4}}$	Distribution in CH_4						Distribution in C_2H_6						
	C_2H_6	D_2					d_0	d_1	d_2	d_3	d_4	M	d_1	d_2	d_3	d_4	d_5	d_6	M
208	6.8	61.2	9	0.02	0.0042	4.70	—	—	2.7	14.2	83	3.8	—	78	1.8	2.6	6.8	10.5	2.7
224	6.8	61.2	9	0.05	0.024	2.04	—	—	8.4	16.7	75	3.7	—	60.9	0.7	5.0	11.0	20.5	3.22
247	6.8	61.2	9	0.1	0.1	1.0	—	5	10	17.0	68	3.5	3.5	42.5	1.2	1.1	12.1	39.5	3.96
156	5.1	46.5	9	0.16	0.017	9.40	3.2	4.0	11.2	16.8	64.8	3.3	15.3	50.4	2.3	2.9	10.3	18.6	2.8
185	5.1	46.5	9	0.69	0.18	3.83	2.4	4.2	15.3	18.9	59.1	3.3	5	45.0	2	3	15	30	3.7
200	5.1	46.5	9	1.15	0.66	1.73	3.2	4.2	15.8	23.4	53.3	3.2	—	35.6	—	3.6	23.1	37.3	4.2
174	7.8	15.8	2	0.36	0.038	9.8	—	—	15.4	30.7	53.8	3.4	—	37	—	3.5	17.9	41.1	4.3
208	7.9	15.8	2	—[a]	1.2	—	—	1.9	14	33.1	51	3.3	—	—	—	—	—	—	—
263	7.9	15.8	2	—[a]	36.2	—	4.3	17	30.5	31.6	16.5	2.6	—	—	—	—	—	—	—
240	6.8	14.5	2.3	4.7	8.9	0.53	0.3	13	31.2	19.9	35.7	2.8	9	29	13.5	16.7	18.1	14.9	3.5
182	6.8	14.5	2.3	0.47	0.1	4.7	—	—	9.2	15	75.2	3.6	—	36.7	—	3.4	16.2	43.8	4.3
242	3.9	12.4	3	2.9	4.5	0.64	—	—	25.3	35.4	51.9	3.6	5.1	36.1	1.4	7.8	22.4	26.9	3.8
242	3.9	39.4	10	1.7	1.3	1.31	—	0.7	5.97	14.9	78.3	3.8	6.8	23.4	—	—	8.2	61.5	4.6

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[a] Exchange reaction is so fast that it cannot be measured precisely.

can be seen. Two nickel catalysts of different specific activity (see rows 1–3 and 4–13) were used characterized by the initial rate of methane formation (column 6). Column 7 shows the ratio of the initial rates of methane formation to that of ethane exchange. In column 8–20 the initial distribution of deuterium atoms in methane and ethane and the mean deuterium number M are presented.

The M value of methane is relatively high due to the high percentage of methane-d_4. With increasing temperature the M value of methane decreases regardless of the different activity levels (see rows 1–3 and 4–6) and of the different hydrogen–ethane ratio (see rows 3–6 and 7–10). This decrease in M is a consequence of the formation of methane containing less deuterium atoms. The ratio found in column 7 is also reduced at high temperature.

All the distributions refer to the initial stage of hydrogenolysis because later the M value in methane decreases due to the dilution of deuterium by ethane exchange. In order to prove it, an experiment was carried out on an extremely active catalyst at 240°C. The distribution of methane was experimentally measured and it was calculated in the following way. It was assumed that first ethane exchange had achieved equilibrium. The distribution of deuterated ethane can be calculated by the binomial expansion. By using these percentage data the distribution of methane could be calculated if we consider the reaction of all these species separately with HD (at equilibrium the deuterium atoms are present in form of HD). Fig. 4 shows the experimental and theoretical distributions calculated in this way.

The same effect was found with tritium-labelled hydrogen. In Table 3 experimental data with tritium are presented. It seems that temperature affects the specific radioactivity of the methane formed in the same sense as the M value varied in the reaction with deuterium, although the activity level of the nickel catalyst is different. The quantity which appears in column 2 can be directly compared to the M value for methane if this latter quantity is divided by 2 (the "specific" deuterium content of carrier free deuterium gas is obviously 2). The values obtained with tritium are a little higher than those with deuterium.

The isotopic content of methane can be influenced by altering the activity of the nickel catalyst and this effect is similar to that of temperature. Freshly made catalyst loses its activity successively and as a consequence the isotopic content of methane increases. The results of these experiments for tritium are summarized in Table 4.

Similarly the deuterium content of

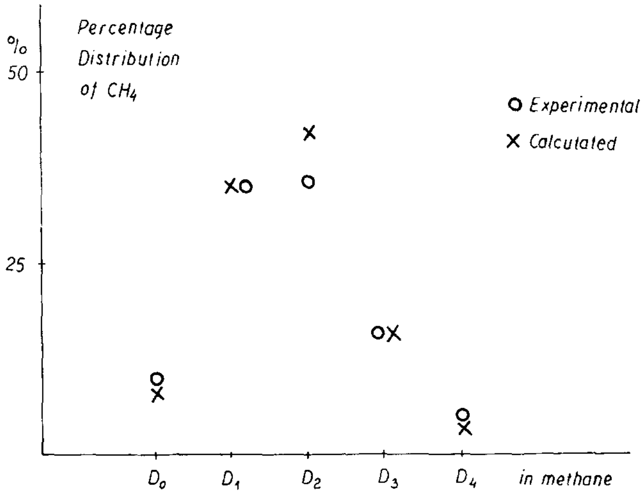

FIG. 4. Percentage distribution of deuterated methane formed during the hydrogenolysis at isotope equilibrium condition. ○ Experimental × Calculated.

TABLE 3

Initial mixture	°C	$p^0_{CH_4}/p^0_{HT}$	$\frac{W^0_{EXCH.}}{W^0_{CH_4}}$	$W^0_{EXCH.}$ % min^{-1}	$W^0_{CH_4}$ % min^{-1}
$p_{C_2H_6} = 60$ Torr; $p_{HT} = 100$ Torr	278	2	6.1	0.092	0.014
	282	2	6.5	0.12	0.0185
	310	1.8	3.0	0.3	0.102
	315	1.7	1.9	0.3	0.156
$p_{C_2H_6} = 40$ Torr; $p_{HT} = 80$ Torr	278	1.97	—	—	—
	310	1.82	—	—	—

methane is always higher on a catalyst possessing a lower activity level reflected in the change of M values. The distribution of differently deuterated species also changes and on catalyst of lower activity the formation of CD_4 is preferred. This behavior is presented in Table 2 if one compares the first three experiments (activity of catalyst lower) with the second three runs.

TABLE 4[a]

No. of run	$W^0_{EXCH.}$ % min^{-1}	$W^0_{CH_4}$ % min^{-1}	$\frac{W^0_{EXCH.}}{W^0_{CH_4}}$	$\frac{p^0_{CH_4}}{p^0_{HT}}$
2	2.36	0.5	4.7	0.91
3	1.42	0.2	7.1	1.1
5	0.76	0.09	8.0	1.3
7	0.61	0.07	8.7	1.9

[a] T = 194°C; $p_{HT} = 19.5$ Torr; $p_{C_2H_6} = 16.5$ Torr.

Finally, we briefly report the results of methane exchange with deuterium. In the same temperature range the main products were methane-d_1 and methane-d_4. The activation energy measured between 208 and 260°C is 30 kcal $mole^{-1}$ in agreement with earlier data (*15*). At 240°C the initial rate of methane-d_4 formation is 0.6% min^{-1}, which is about 15 times less than the value obtained for methane formation on catalyst of the same activity (see Table 2, row 10, column 6). If the hydrogenolysis is carried out in the presence of added methane, neither the distribution nor the M value of methane formed is altered.

DISCUSSION

Generally it can be established that the lower end of the temperature interval for hydrogenolysis is about 40°C higher than that of ethane exchange. Methane is the sole product and its formation takes place with measurable rate between 180 and 300°C depending on the activity level of the catalyst. All the reactions were carried out in the presence of excess hydrogen, so the possibility of formation of carbon deposit is negligible and this is supported by the carbon balance.

Kinetics

The results obtained in the present work are in good agreement with those of Sinfelt and Taylor (*14*) as well as of Shephard (*9*). The hydrogenolysis is inhibited by hydrogen at low temperature whereas the order with respect to ethane is 1. At enhanced temperature the order of reaction with respect to hydrogen increases and eventually the methane formation becomes independent of the hydrogen pressure in the gas phase. The exponent of the ethane pressure decreases to a small extent. Methane present in the initial hydrogen–ethane mixture does not influence the hydrogenolysis either at low or at high temperature.

The effect of hydrogen can be explained in such a way that its coverage decreases on the surface as the temperature increases (*23*) and so the number of sites responsible for the dissociative adsorption of ethane increases. Methane behaves as an inert diluent, so its adsorption between 180 and 253°C may be neglected. This latter statement is supported by the experimental data on methane exchange with deuterium and tritium (*11*) showing that this process is much slower than the methane formation in hydrogenolysis.

The results of the present work concerning the order of reaction give a strong confirmation for the revised kinetics of Sinfelt obtained for ethane hydrogenolysis over cobalt-on-silica catalyst rather than the original kinetics described by Cimino, Boudart and Taylor (*1*). These latter cannot explain the increasing exponent of hydrogen with increasing temperature.

According to Sinfelt and Taylor (*14*)

$$w = (k_1 \cdot p_{C_2H_6})/(1 + b \cdot p_{H_2}) \qquad (1)$$

where k_1 is the rate constant of ethane adsorption and b is proportional to the ratio of the rate constant of ethane desorption and that of the C–C bond rupture. According to the data in Table 2 (column 7, rows 1–6, 10, 11), the initial rate of formation of deuterated ethane (which is characteristic of ethane desorption) increases to a lesser extent than that of methane formation with increasing temperature. This is equivalent to the decrease of b (provided the coverages change proportionately in both cases) and finally zero order kinetics with respect to hydrogen can be obtained.

The apparent activation energy is comparable to those found in the literature. Unfortunately, the value is influenced by many factors so no conclusion can be drawn from these data. The significant difference which has to be emphasized is that among the energies of activation obtained for hydrogen exchange in the ethane molecule (18–20 kcal mole^{-1}) (*16*), for hydrogen exchange in methane molecules, viz. 33 (*11*) and 30 kcal mole^{-1} with tritium and deuterium respectively, and for ethane hydrogenolysis (37–39 kcal mole^{-1}).

Mechanism

The application of isotopes to hydrogenolysis may give more information about the hydrogen content of surface radicals or, at least, the migration of hydrogen atoms among the different species.

The following equations have to be taken into account. Earlier it was proved that in ethane exchange the initial step is the dissociative adsorption of ethane by 1,2- diadsorbed species (*16*).

$$C_2H_6(g) \rightarrow C_2H_4(a) + 2H(a) \qquad (2)$$

where (g) and (a) denote the species in the gaseous and adsorbed states, respectively. The desorption of C_2H_4(a) radicals leads to the ethane-d_2 molecule which is one of the main products of ethane exchange with deuterium. However, this radical suffers further exchange on the surface without leaving it and in this way highly deuterated radicals are formed on the catalyst:

$$C_2H_4(a) \xrightarrow{-H} C_2H_x(a) \xrightarrow{+D} C_2H_yD_{4-y}(a) \qquad (3)$$

This process is preferred at high temperature and so perdeuterated ethane forms.

Simultaneously the rupture of the C–C bond takes place

$$C_2H_4(a) \rightarrow C_2H_x(a) \rightarrow 2CH_z(a) \qquad (4)$$

The hydrogenation of monocarbon fragments is the last step and this leads to methane

$$CH_z(a) + (4\text{-}z)H(a) \rightarrow CH_4(g) \qquad (5)$$

Before the desorption, however, the monocarbon fragments may undergo further exchange with deuterium or tritium represented by the following equation:

$$CH_z(a) + D(a) \rightarrow CH_{z-u}D_u(a) + uH(a) \qquad (6)$$

By using Eq. (2) we assume that the initial step for hydrogenolysis is the dehydrogenation of the ethane molecule similarly to that of ethane exchange. This is opposite to what Anderson and Baker (*8*) found since they put forward the ethane adsorption with C–C bond rupture. This mechanism might be valid for nickel film but in our work the lack of CH_3D as main product shows that adsorption with C–C bond rupture is not favourable. Since the methane exchange is slow the absence of CH_3D cannot be attributed to the surface exchange of methyl radicals.

Calculation of the energy requirements for the two types of adsorption also gives support for initial dehydrogenation. For the adsorption given by Eq. (2) it is:

$$Q_{CH,Ni} = 2Q_{CH} - 2Q_{HNi} - 2Q_{CNi} \qquad (7)$$

and for adsorption of $C_2H_6(g) \rightarrow 2CH_3(a)$ it is

$$Q_{C-C,Ni} = Q_{C-C} - 2Q_{CNi} \quad (8)$$

Taking the values of 96, 83, (*17*) 21, (*18*) and 60 kcal $mole^{-1}$ (*19*) for Q_{CH}, Q_{C-C}, Q_{CNi}, and Q_{HNi} respectively, $Q_{CH,Ni}$ is 30 and $Q_{C-C,Ni}$ is 41 kcal $mole^{-1}$. We should emphasize that the absolute values are not to be considered as a correct measure of the heats of these endothermic surface interactions. The only fact to be illustrated by this difference is that the adsorption with hydrogen dissociation from ethane is energetically more favourable.

Kinetic evidence has been shown that the rate-limiting step is the C–C bond rupture as represented by Eq. (4). Consequently, the desorption of methane is faster than this latter process. In order to confirm this the following experimental facts have to be considered. First, the methane has no influence on the hydrogenolysis of ethane, so surface radicals resulting from methane [reverse step in Eq. (5)] can be neglected. Moreover, if the methane desorption had been the slow step, the quantity of surface radicals formed according to Eq. (2) and Eq. (4) would be increased with increasing temperature leading to the increase of deuterated methane characterized by Eq. (6). The data in Table 2, however, show the opposite trend irrespective of catalyst activity (see Table 2, column 13, rows 12, 13 and 1–3, 4–6) and of the composition of the initial gas mixture (rows 4–6 and 7–10). Second, it was shown earlier (*20–22*) that methane adsorption accompanied by the rupture of the C–H bond is the rate-determining step in methane exchange. Since this adsorption step is endothermic the activation energy for methane desorption should be smaller than that for adsorption. Since the energy of activation for methane exchange is 30–33 kcal $mole^{-1}$ measured under the same experimental condition as the hydrogenolysis, the activation energy for methane desorption should be lower than that for hydrogenolysis.

Explanation is needed for the change of the initial distribution and *M* values of methane formed and those of ethane as the temperature and the catalyst activity are changing. First of all, we have indirect confirmation that the distribution of deuterated methane reflects the state referring to the hydrogen content of the radical at which the breaking of the carbon–carbon bond takes place. In the present experiments it was found that the formation of perdeuterated methane in methane–deuterium exchange is much less than the formation of methane in the ethane hydrogenolysis at the same temperature. This result shows that the high amount of methane-d_4 may not be accounted for by Eq. (6) and so after the C–C bond break there is no further change in isotope composition of methane.

M values (column 13 and 21) change in the opposite direction, and the same is valid for methane-d_4 and ethane-d_6. This can be explained in the following way: During the course of surface exchange [Eq. (3)] one can find radicals on the surface denoted by C_2H_x(a) the deuterium content of which changes from 0 to x. At lower temperature (see Table 2 rows 1, 4, 11, Table 3 row 1) the process characterized by Eq. (3) repeatedly occurs and finally the desorption of this radical produces ethane-d_6 or after C–C bond rupture CD_4 is formed. By increasing the temperature the process denoted by Eq. (4) takes place much faster; therefore the rupture of the C–C bond occurs at lower deuterium content of C_2H_x and this competition is an explanation for the decreasing deuterium content in methane.

The same effect can be observed with the change in catalytic activity of nickel. By comparing the data at the same temperature (Table 2 rows 6, 12, 13 and Table 4) it is clear that the lower the activity of the catalyst the higher is the *M* value or $\rho^0_{CH_4}/\rho^0_{HT}$.

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