

The Kinetics of the Catalytic Hydrogenolysis of Ethane over Ni/SiO₂

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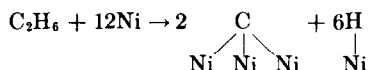
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Received July 31, 1978; revised May 10, 1979

The rate of hydrogenolysis of ethane over a Ni/SiO₂ catalyst, studied over a large range of pressure and of temperature, is shown to be related to the degree of hydrogen coverage θ_H , by the equation:

$$r = k_0 P_{C_2H_6} e^{-E_0/RT} \theta_H^Y (1 - \theta_H)^X$$

with k_0 nearly equal to the number of ethane molecules colliding with the Ni surface, $E_0 = 14 \pm 1$ kcal/mole, $Y = -1 \pm 2$ and $X = 15 \pm 2$. The rate-limiting step is believed to be the irreversible, dissociative adsorption of ethane on an ensemble of at least 12 adjacent Ni atoms, free from adsorbed hydrogen, resulting in the complete cracking of C₂H₆:



Irreversible adsorption of ethane is assumed to compete with the reversible adsorption of hydrogen. This mechanism, which is compared with those proposed earlier, is in good agreement with data on ethane adsorption studied by magnetic methods, and with a study of ethane hydrogenolysis over Ni-Cu/SiO₂ catalysts.

INTRODUCTION

In a number of catalytic reactions involving hydrogen and hydrocarbons, such as hydrogenolysis, isomerization, and deuterium exchange, the pressure of hydrogen generally has an inhibiting effect. Among these reactions, hydrogenolysis of ethane has received considerable attention (1, 2), and various mechanisms, essentially derived from kinetic studies, have been proposed: It was first assumed (3) that ethane is reversibly adsorbed as a dehydrogenated species, thus accounting for negative orders versus hydrogen, and that the rate-determining step is the subsequent C-C bond scission. This kinetic scheme was modified by Sinfelt (4) to give a better fit to new kinetic data.

Kemball (5), however, has criticized this model in which the competition between

adsorbed hydrogen and adsorbed hydrocarbon was not considered, and has proposed another mechanism taking these effects into account. Another objection was raised by Boudart (6) who criticized the reversibility of the dissociative adsorption of ethane assumed in the early model. Ethane adsorption, the rate-controlling step in the mechanism suggested by this author, was supposed to be irreversible. Moreover, the hydrocarbon ad-species, strongly dehydrogenated on two types of sites, was assumed to be in competition with the reversibly adsorbed hydrogen. This mechanism results in an equation where the rate is a function of $(1 - \theta_H)^y$, θ_H being the hydrogen coverage, and y the number of H atoms lost by the hydrocarbon upon adsorption.

Frennet *et al.* (7), by comparing ethane

hydrogenolysis with methane and ethane deuterium exchange, have proposed a mechanism in which the hydrogenative desorption of adsorbed C1 fragments is the rate-controlling step, as already suggested by Anderson (2). The rate equation thus obtained applies particularly well to the case of Ru, Rh, and W. On Ni, however, no clear conclusion could be drawn. In an improved scheme, which does not imply any exact mechanism, Frennet *et al.* (8) have suggested that both reactants are in competition on the same sites, as in Kemball's model, and that the adsorbed hydrocarbon, which in this model is only slightly dehydrogenated, needed a patch of Z-free first neighboring sites. According to this model, the rate of adsorption, which should be related to the rate of reaction, is proportional to $(1 - \theta_H)^2$. This expression is similar to that proposed earlier by Boudart (6). The exponent, however, does not have the same physical meaning.

The preceding brief review shows that the mechanism of ethane hydrogenolysis as deduced from kinetic studies is far from being completely unequivocal.

Hydrocarbon adsorption studies have been carried out in this laboratory (9, 10) on Ni and Ni-Cu alloys with magnetic methods. Results thus obtained have allowed us to formulate some hypotheses on the mechanism of ethane hydrogenolysis (11). They can be summarized in the following way:

(i) Two adsorbed ethane species are detected on nickel: The first one, stable between 260 and 293°K, involves six Ni atoms and corresponds to a partial dehydrogenation of the molecule without C-C bond rupture (hydrogenation yields back gaseous ethane). The second adspecies is observed above 345°K and requires 12 surface Ni atoms (9). Since this species is the only one which gives methane by hydrogenation (11), it was postulated that this species

could be the intermediate in ethane hydrogenolysis (11).

(ii) Addition of Cu to Ni by alloying strongly inhibits the formation of both species. It was suggested that Cu atoms, inactive for chemisorption, act as a diluent of active nickel atoms, so that the number of ensembles composed of 6 or 12 adjacent Ni atoms decreases with alloying (11).

(iii) Chemisorbed hydrogen atoms also play the role of an inhibitor with respect to ethane adsorption. It was suggested that the inhibiting effect of hydrogen in the hydrogenolysis reaction could originate, as in the case of Cu atoms, from a dilution phenomenon (11).

The aim of the present study was to determine a quantitative relation between the rate of hydrogenolysis and the number of ensembles of X neighboring nickel atoms free from hydrogen, which is directly correlated with the $(1 - \theta_H)^x$ function. Hydrogen adsorption on a well-defined Ni/SiO₂ catalyst was determined under various conditions of temperature and H₂ pressure, and then the rate of hydrogenolysis of ethane was measured for the same conditions.

EXPERIMENTAL

The Ni/SiO₂ catalyst (23% weight Ni) was prepared by reduction in a hydrogen stream at 920°K for 15 hr of a precursor prepared by the addition of SiO₂ (Aerosil Degussa, 200 m²/g) to a solution of nickel nitrate hexammine (12). Pore size radii deduced from a nitrogen adsorption-desorption isotherm at 77°K were 13.5 nm. The BET surface area was 250 m²/g and the micropore volume was 0.96 ml/g. Magnetic methods have demonstrated that reduction was almost complete and that the average surface diameter of the nickel particles was 6.4 nm (12, 13). Hydrogen adsorption experiments were performed after outgassing the reduced catalyst under 10⁻⁶ Torr at 750°K for 1 hr. The volume

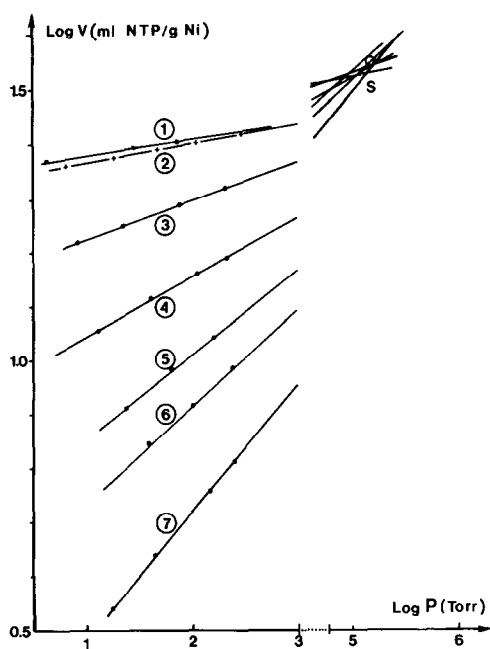


FIG. 1. Log-log isotherms for H₂ adsorption on Ni/SiO₂ at 195, 256, 420, 509, 570, 640, and 793°K (curves 1 to 7).

of adsorbed gas was measured in a classical volumetric apparatus equipped with a pressure gauge (Texas Instruments).

The reaction studies were carried out in a flow system with a fixed-bed reactor at atmospheric pressure. The microreactors were quartz tubes (diameters from 0.4 to 0.8 cm) and samples (from 0.018 to 0.3 g) were held in place by quartz wool. A chromel-alumel thermocouple held in a coaxial sheath measured the temperature which remained constant to $\pm 1^\circ\text{C}$. The catalyst (diameter of particles, ca. 0.1 mm) was reduced *in situ*, in conditions similar to those used for adsorption experiments. Conversions were always smaller than a few percent. The total flow at room temperature was 120 ml/min, and in most experiments the ethane partial pressure was ca. 6 Torr. For these conditions we ascertained that diffusion was not rate limiting (14). Hydrogen and the diluent, helium (initial purity better than 99.99%), were further purified by a Dcoxo catalyst fol-

lowed by a zeolite trap. Purity of ethane was better than 99.9%. Gas analyses were performed by gas chromatography with a flame-ionization detector.

RESULTS

Hydrogen Adsorption

After each admission of hydrogen, the steady equilibrium pressure was rapidly attained. As already noted by Schuit and de Boer with completely reduced Ni/SiO₂ catalyst (15), no significant activated chemisorption was observed. Successive hydrogen doses were injected every 10 min. The desorption isotherm at room temperature coincided with the adsorption isotherm at the same temperature. After two adsorption outgassing cycles, the reproducibility of the measurements was better than 2%. As seen in Fig. 1, from 10 to 300 Torr the data are best represented by the Freundlich relation, $V = kP^a$. The exponent a varies linearly from 0.04, at 350°K, to 0.25 at 800°K.

All isotherms in Fig. 1 converge to point S which can be considered as characterizing

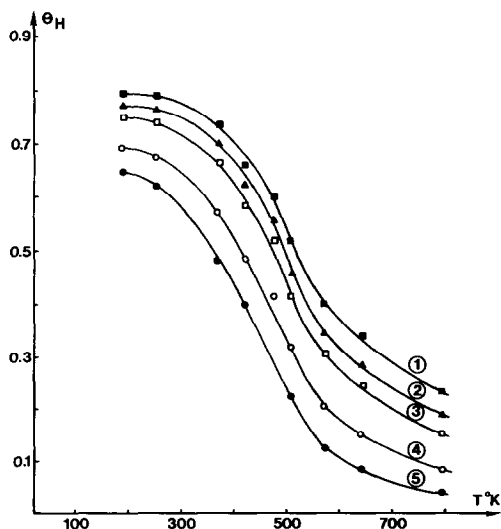


FIG. 2. Isotherms for H₂ adsorption on Ni/SiO₂ at 660, 300, 100, 10, and 1 Torr (curves 1 to 5).

saturation of the surface (16). The corresponding adsorbate volume is 34.5 ml NTP/g Ni, and can be used to calculate the nickel particle diameter. In the calculation, it was assumed that particles are spherical, as suggested by electron micrographs, and exhibit (100) and (111) planes at their surface. The result (6.3 nm) is in excellent agreement with the diameter deduced from magnetic measurements (6.4 nm).

Various isobars are presented in Fig. 2. Isothermic heats (Fig. 3) are in reasonable agreement with calorimetric data (17).

Kinetic Data

Catalyst-ageing phenomena were not observed and in typical experimental conditions, the rate decrease was smaller than 5% after 10 hr. Moreover, after a change of reactant pressure (hydrogen or ethane) or temperature, the original rate was restored when the initial conditions were reestablished.

At 527°K, with $P_{H_2} = 550$ Torr, the partial reaction order with respect to the pressure of ethane was 1.0 below 10 Torr and 1.6 above it, as illustrated in Fig. 4. Similar results were obtained for other temperatures and hydrogen pressures. To

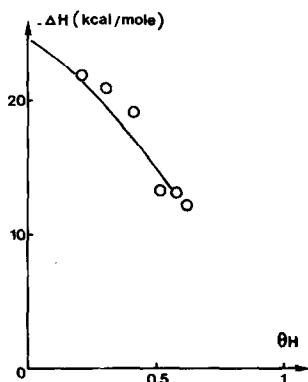


FIG. 3. Heat of adsorption of H_2 on Ni/SiO_2 : solid curve, calorimetric data (Ref. 17); open circles, isothermic heat.

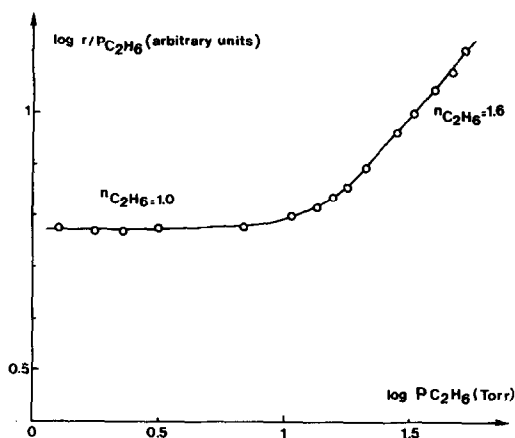


FIG. 4. Partial reaction orders with respect to ethane pressure at 527°K and 550 Torr H_2 [$\log (r/P_{C_2H_6})$ against $\log P_{C_2H_6}$].

our knowledge, reaction orders higher than unity have never been reported for this reaction with nickel catalysts. However, re-

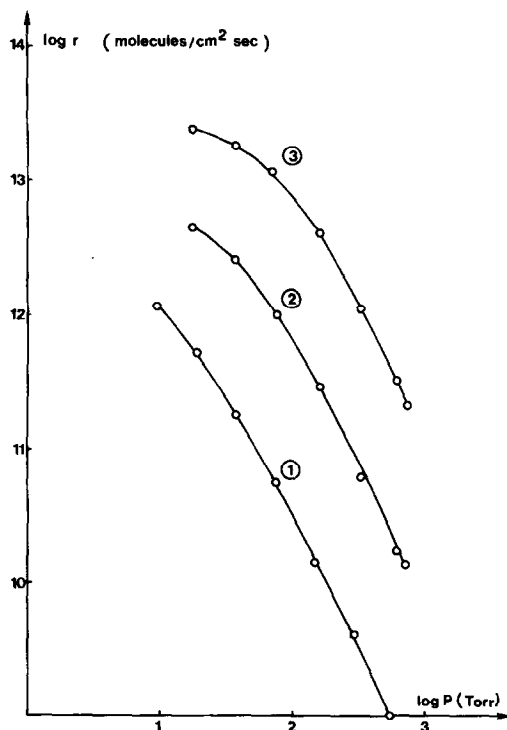


FIG. 5. Partial reaction orders with respect to hydrogen pressure (slopes of $\log r$ against $\log p$ curves) at 456, 507, and 538°K (curves 1, 2, and 3). (Catalysts weights were varied from 0.292 to 0.018 g to cover the whole temperature range.)

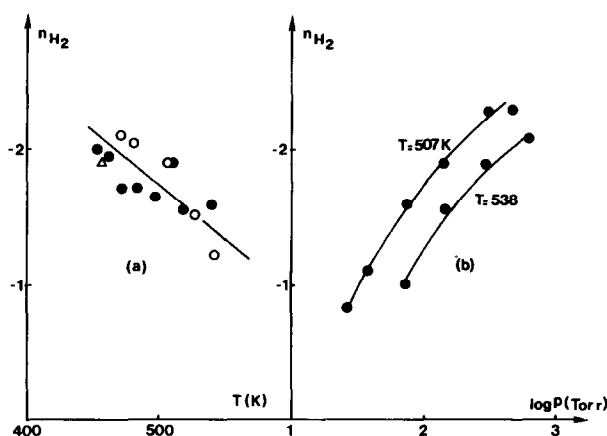


FIG. 6. Variations of partial reaction orders with respect to hydrogen with temperature at 160 Torr H₂ (a) and with hydrogen pressure (b). Weight of catalyst: 0.018, 0.092, and 0.292 g for open circles, triangles, and filled circles, respectively.

action orders as high as 1.2 have been recently observed by Barbier *et al.* (18) with Pt catalysts.

High values of the reaction orders could be explained by some bimolecular processes involving a reaction between a gaseous C₂H₆ molecule and an adsorbed hydrocarbon species. This unexpected behavior will require further investigation. The present study has been restricted to the region where the order is equal to unity: In what follows, the hydrocarbon pressure has been maintained constant at 6 Torr.

In Fig. 5, conversion rates are plotted against hydrogen pressure, P . Partial reaction orders with respect to hydrogen, n_{H_2} , are negative, as previously observed (1-3). Moreover, they vary with temperature, in agreement with some published data (19), and with the hydrogen pressure (Fig. 6). The apparent activation energy, E_a , also varies with temperature and hydrogen pressure (Fig. 7): Apparent activation energy and order with respect to hydrogen both decrease when temperature increases and when hydrogen pressure decreases.

Correlation of r with θ_H

Let us suppose that the following relation holds between the reaction rate, r , and

the hydrogen coverage, θ_H

$$r = k(1 - \theta_H)^x, \quad (1)$$

when the partial pressure of ethane is maintained constant. [Preliminary calculations (20), based on hydrogen chemisorption data obtained with a Ni/SiO₂ catalyst

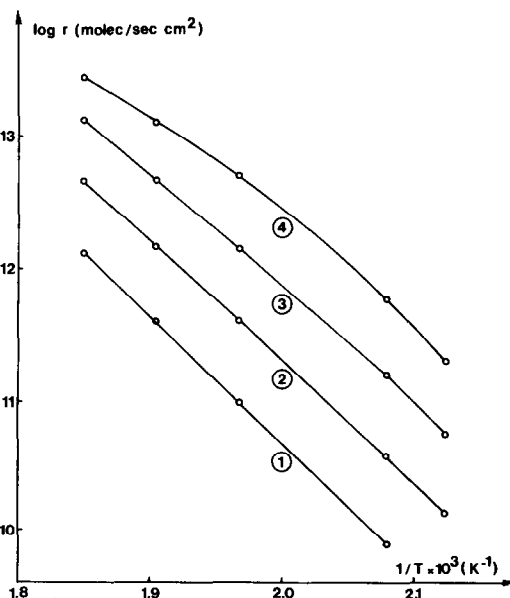


FIG. 7. Arrhenius plot for hydrogen partial pressures equal to 660, 310, 160, and 80 Torr (curves 1 to 4).

studied in the laboratory, and based on previously published kinetic data for hydrogenolysis, have shown that this type of approach yields correct orders versus hydrogen and apparent activation energies, provided the value of the exponent, X , is large enough, for instance $X = 12$.]

Let us also assume that k and X are independent of hydrogen pressure, P . Writing that the partial reaction order with respect to hydrogen pressure

$$n = \left(\frac{\partial \log r}{\partial \log P} \right)_T = \left(\frac{\partial \log r}{\partial \log \theta_H} \right)_T \left(\frac{\partial \log \theta_H}{\partial \log P} \right)_T$$

and differentiating

$$\log r = \log k + X \log (1 - \theta_H),$$

we arrive at Eq. (2):

$$n/a = -X\theta_H/(1 - \theta_H), \quad (2)$$

where $a = (\partial \log \theta_H / \partial \log P)_T$ is the slope of the Freundlich transform and is also the exponent of the relation $V = kP^a$. As can be seen in Fig. 1, the exponent a is, as a first approximation, independent of P . It can be easily shown that if Eq. (2) holds, then Eq. (1) is verified. It should be added that if the rate is given by:

$$r = k(1 - \theta_H)^X \theta_H^Y, \quad (1')$$

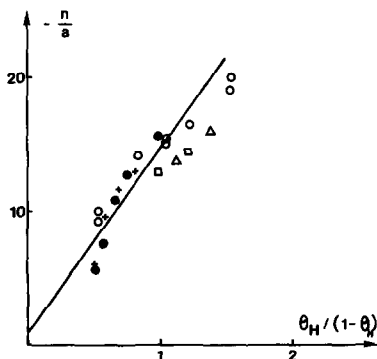


FIG. 8. Correlation between the order for H_2 and the degree of hydrogen coverage of Ni: n/a against $\theta_H/(1 - \theta_H)$ at 456°K (open circles), 469°K (triangles), 483°K (squares), 507°K (crosses), and 538°K (filled circles).

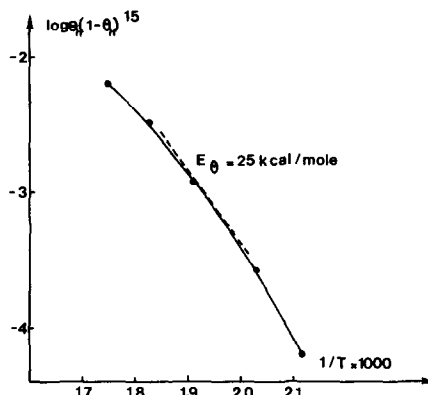


FIG. 9. $\log \{\theta_H^{-1}(1 - \theta_H)^{15}\}$ as a function of $1/T$.

then:

$$n/a = Y - X\theta_H/(1 - \theta_H). \quad (2')$$

If Eqs. (1) or (1') are valid, one should obtain a straight line by plotting n/a at a given temperature for various hydrogen pressures, against $\theta_H/(1 - \theta_H)$. Such plots are presented in Fig. 8 from which it can be deduced that $Y = -1 \mp 2$ and that X , which is temperature independent in the range studied, is 15 ∓ 2 . The experimentally determined orders, and their variations with temperature and hydrogen pressure are thus *quantitatively* accounted for, if the following rate law is assumed:

$$r = kP_{C_2H_6} \theta_H^{-1}(1 - \theta_H)^{15}, \quad (3)$$

k and $\theta_H^{-1}(1 - \theta_H)^{15}$ are temperature dependent. k may be written as:

$$k = k_0 e^{-E_0/RT}, \quad (4)$$

where E_0 is the true activation energy. As illustrated in Fig. 9, $\theta_H^{-1}(1 - \theta_H)^{15}$ varies as $e^{-E_\theta/RT}$ in a small temperature range. The observed apparent activation energy is thus equal to:

$$E_a = E_0 + E_\theta.$$

At 493°K, when $P = 310$ Torr, $E_a = 40 \mp 2$ kcal/mole (1 cal = 4.18 J) and $E_\theta = 25 \mp 2$ kcal/mole (Fig. 7). Hence, $E_0 = 15 \mp 4$ kcal/mole.

There is another way to determine E_0 with a better accuracy. It is based on the

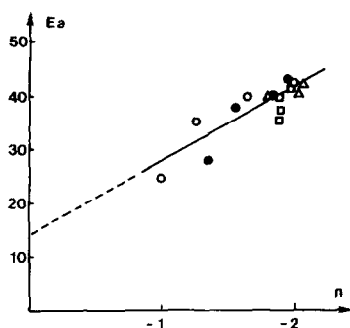


FIG. 10. Apparent activation energy against observed order for hydrogen: filled circles, $T = 540^\circ\text{K}$; open circles, $T = 525^\circ\text{K}$; squares, $T = 508^\circ\text{K}$; and triangles, $T = 271^\circ\text{K}$.

fact that there should exist a simple relation between E_θ (and hence E_a) and n , since both originate from the same expression, $\theta_H^Y (1 - \theta_H)^X$. This equation (see the Appendix) is:

$$E_\theta = -nQ_{\text{iso}}$$

$$E_a = E_0 - nQ_{\text{iso}}$$

where $Q_{\text{iso}} = -R(\partial \log P / \partial 1/T)\theta_H$ is the isosteric heat of hydrogen adsorption for the hydrogen coverage corresponding to the conditions at which E_a and n are measured. These equations explain the parallel variations of E_a and n with T and P which are indeed observed.

Q_{iso} can be considered to a first approximation to be nearly constant and equal to 15 kcal/mole (actually it varies from 12 to 18 kcal/mole for the extreme conditions of temperature and pressure used here). Hence, by plotting E_a against the corresponding value of n , one should observe a straight line whose intercept with the vertical axis and slope should be respectively equal to E_0 and Q_{iso} . This is indeed observed (Fig. 10); the calculated slope is equal to 14 kcal/mole and the calculated value for E_0 , 14 kcal/mole, in agreement with the previously determined value. The true activation energy, E_0 , being known, it is possible to calculate k_0 from Eq. (4). The calculated rate at 507°K

($P = 160$ Torr, $P_{\text{C}_2\text{H}_6} = 6.3$ Torr) is equal to 0.08×10^{13} molecules/cm² Ni/sec (average of three determinations). The corresponding θ_H is 0.434. The constant k_0 is then equal to 0.16×10^{22} molecule/cm² Ni/sec/Torr.

It is of interest to compare k_0 with the number ν of ethane molecules colliding with a unit surface area of nickel per second and per Torr of ethane at about 500°K . The value deduced from the kinetic theory of gases ($\nu = 3.5[P(\text{Torr})/(MT)^{1/2}] \times 10^{22}$ molecules cm⁻² sec⁻¹; M , molecular weight; T , temperature) is $\nu = 0.03 \times 10^{22}$, five times smaller than k_0 . A difference of 1.6 kcal/mole on E_0 or of 3 on X , within the uncertainty range of their determination, would lead to identical values for k_0 and ν . Hence, to a first approximation, it will be considered that k_0 is nearly equal to the number of ethane collisions on the nickel surface.

The present study has therefore demonstrated that the rate expression which accounts for the observed variations of the rate with temperature and the reactant partial pressures, can be written as:

$$r = k_0 P_{\text{C}_2\text{H}_6} e^{-E_0/RT} \theta_H^Y (1 - \theta_H)^X, \quad (5)$$

where $k_0 = 0.16 \times 10^{22}$ molecule/cm² Ni/sec/Torr, $E_0 = 14 \pm 1$ kcal/mole, $Y = -1 \pm 2$, and $X = 15 \pm 2$.

DISCUSSION

In Eq. (5), the function $(1 - \theta_H)^X$ represents the probability of finding at least X adjacent nickel atoms free from adsorbed hydrogen. Therefore, the rate, r , is proportional to the number of such ensembles on the surface.

This conclusion has been confirmed in this laboratory by Dalmon (21) in the course of a study of ethane hydrogenolysis on silica-supported Ni-Cu alloys. The surface composition of these alloys studied by volumetric hydrogen titration and magnetic methods (22) was found to be very similar to the bulk one, in contrast with the

surface enrichment in copper generally observed on unsupported powders and films.

The rate of hydrogenolysis, measured in standard conditions, was found to vary with copper concentration (Cu), as:

$$r = k' [1 - (\text{Cu})]^N \quad (6)$$

with $N = 12 \mp 2$.

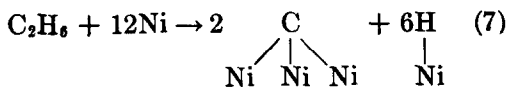
Now, $[1 - (\text{Cu})]^N$ is the probability of having an ensemble of at least N adjacent nickel atoms, if it is assumed that there is no short range ordering of nickel and copper at the surface.

The fact that X and also N are both nearly equal to the number of nickel atoms involved in the dissociative adsorption of ethane as



(as deduced from magnetic methods) strongly suggests that the intermediate in ethane hydrogenolysis is this species, in agreement with our earlier hypothesis (11).

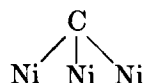
This allows further speculations on the mechanism of the reaction: Our data indicate that k_0 , the hydrogenolysis rate constant, is of the same order of magnitude as ν , the number of ethane collisions on the nickel surface, and that the reaction partial order with respect to ethane is unity in a large pressure range. The simplest mechanism which these observations suggest is a mechanism according to which the rate-determining step could be the irreversible adsorption of ethane as:



with, in addition, a competitive, reversible adsorption of hydrogen. Equation (7) should be considered as a bimolecular process between C_2H_6 and ensembles of at least 12 adjacent free nickel atoms, considered as a reacting site in the sense of Frennet *et al.* (8). The true activation

energy, E_0 , of ethane hydrogenolysis, which has been found to be 14 kcal/mole, would then correspond to the activation energy of adsorption (Eq. 7).

In the proposed mechanism, it is implicitly assumed that hydrogenation of the surface carbidic species



is fast compared with the adsorption of ethane. The additional following experiment was performed: Ethane was adsorbed (Eq. 7) at 360°K on the catalyst, and the system cooled down. The hydrogenation of the surface species thus formed starts at room temperature, i.e., at a very much lower temperature than the temperature of adsorption.

It is also supposed that during the reaction, the coverage by the surface carbide species, as well as by other adsorbed hydrocarbons which could be active in parallel reactions like exchange, is negligible. This hypothesis is generally proposed when the reaction order with respect to the hydrocarbon is equal to unity (8), as was experimentally observed by Frennet *et al.* (8) in the case of the $\text{D}_2\text{-CH}_4$ exchange reaction.

It is also of interest to compare this mechanism with those already proposed. The mechanisms proposed by Cimino *et al.* (3) and by Sinfelt (4), will not be considered in this discussion since they do not take into account the competition between H_2 and C_2H_6 adsorptions, in contradiction with observed data (11). Furthermore, they have already been critically discussed by Kemball (5), Boudart (6), and Frennet *et al.* (7, 8).

As far as we know, the only complete competitive mechanism proposed earlier is that of Boudart (6) [it should be recalled at this point that Kemball (5) and Frennet *et al.* (8) have not presented a precise mechanism for hydrogenolysis, but they

have characterized ethane adsorption in the presence of hydrogen, which could be related to the catalytic hydrogenolysis reaction]. In the Boudart mechanism, it is assumed that hydrogen is dissociatively chemisorbed in equilibrium with sites S, which are considered as nearly saturated by hydrogen, so that $(1 - \theta_H) = k^{\frac{1}{2}} (H_2)^{\frac{1}{2}}$ (8). Sites S differ from sites (*) on which hydrocarbon is supposed to be irreversibly adsorbed, losing y hydrogen atoms which are adsorbed on neighboring sites. The kinetic equation thus obtained is:

$$r = K' (C_2H_6)^{1-m} (H_2)^m (1 - \theta_H)^{\nu(1-m)} \quad \text{with } 0 < m < 1. \quad (8)$$

In the experimental conditions reported in this study, the partial reaction order with respect to ethane is equal to unity; hence $m = 0$. Then:

$$r = K' (C_2H_6) (1 - \theta_H)^{\nu}. \quad (9)$$

Substituting (8) in (9) yields:

$$r = K'' (C_2H_6) (H_2)^{-\nu/2}. \quad (10)$$

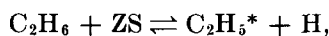
Equation (10) accounts for the observed values of partial orders with respect to hydrogen. For instance, when $y = 4$, then $n = -2$. Equation (10), however, fails to explain variations of the partial order with respect to hydrogen with temperature and pressure, unless it is furthermore assumed that the degree of ethane dehydrogenation increases as the hydrogen pressure increases, and decreases as temperature increases, both hypotheses appearing improbable.

Another weakness of this mechanism is that $(1 - \theta_H)$ is supposed to be proportional to $(H_2)^{-0.5}$. In the conditions of the present study (Fig. 2), $(1 - \theta_H)$ varies as $(H_2)^{-0.2}$. Data reported in Ref. (15) indicate a similar law. Then, in order to account for $n = -2$, one must select a value for y which is too high ($y = 10$). This is clearly impossible.

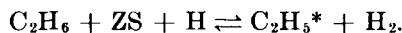
In the present mechanism, high y values are explained with the assumption of only

one type of sites, as in (5) and (8), and with the additional assumption of a complete dehydrogenation and cracking of adsorbed ethane, in competition with hydrogen chemisorption.

In the model of Frennet *et al.* (8) for hydrocarbon adsorption in the presence of hydrogen, both gases are adsorbed on the same nickel sites, as in the present mechanism:



or



At low hydrocarbon coverages, the rate of adsorption is given by:

$$r_{ads} = k (C_2H_6) (1 - \theta_H)^2 \quad (11)$$

or

$$r_{ads} = k (C_2H_6) \theta_H (1 - \theta_H)^2 \quad (12)$$

These equations are formally very similar to that of Boudart and to ours. The exponent, however, does not have the same physical meaning. It results from a partial dehydrogenation in Eq. (10), from a complete dehydrogenation and C-C bond rupture in the mechanism proposed in this paper, and from some steric effect of the $C_2H_5^*$ radical in the model of Frennet *et al.* (8). Moreover, it is more or less implicitly assumed by Frennet *et al.* (8) that adsorption is reversible, at variance with the Boudart's mechanism and ours.

There is another point which deserves some comment: In this work, a quantitative relationship between θ_H , the resulting hydrogen coverage on all nickel surface atoms of the sample, and r , the rate of hydrogenolysis, has been found. This would suggest that all nickel atoms susceptible to react with hydrogen (in fact all the surface nickel atoms) are catalytically equivalent and participate in the reaction. A preliminary study of the structure sensitivity of reaction (12) has shown that the reaction rate expressed per unit surface area first increases slightly, goes through a

flat maximum, then decreases sharply as the average nickel particle diameter increases from ca. 2.5 to 15 nm. The study reported here has been performed on one of the most active samples in order to test the sample with the largest fraction of catalytically active surface. It can moreover be added that on less active samples, we did not succeed in finding a simple relation similar to Eq. (7) between the reaction rate r , and the resulting hydrogen coverage. We may conclude that in these catalysts a small fraction of the nickel surface was active [(111) planes being probably inactive], so that the rate of hydrogenolysis, r , on the active surface fraction is not related to θ_H , the hydrogen coverage on all nickel atoms (23).

The problem, now, is to know whether the kinetic analysis presented here is applicable to other reactions besides hydrogenolysis.

APPENDIX

Suppose that $r = k(T) f(\theta_H)$ and by definition,

$$n = \left(\frac{\delta \log r}{\delta \log P} \right)_{1/T}$$

and

$$E_s = -R \left(\frac{\delta \log P}{\delta (1/T)} \right)_P$$

then

$$E_\theta = -R \frac{d \log f}{d \log \theta_H} \left(\frac{\delta \log \theta_H}{\delta (1/T)} \right)_{r}$$

$$n = \frac{d \log f}{d \log \theta_H} \left(\frac{\delta \log \theta_H}{\delta \log P} \right)_{1/T}$$

and

$$E_\theta = -Rn \left(\frac{\delta \log \theta_H}{\delta (1/T)P} \right) / \left(\frac{\delta \log \theta_H}{\delta \log P} \right)_{1/T}$$

Furthermore the following relation holds:

$$\begin{aligned} \left(\frac{\delta \log \theta_H}{\delta (1/T)} \right)_P / \left(\frac{\delta \log \theta_H}{\delta \log P} \right)_{1/T} \\ = - \left(\frac{\delta \log P}{\delta (1/T)} \right)_{\theta_H} \end{aligned}$$

In order to demonstrate this one must consider that $\log \theta_H$ is a function of $1/T$ and $\log P$, and that $\log P$ is a function of $1/T$ and θ_H . $d \log \theta_H$ and $d \log P$ can be calculated and substitutions yield the relation given above.

Finally, one obtains:

$$E_\theta = -nQ_{iso}$$

and

$$Q_{iso} = -R \left(\frac{\delta \log P}{\delta (1/T)} \right)_{\theta_H}$$

These relations hold whatever $f(\theta_H)$.

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