(5) The selectivity in hydrogenolysis parallels very closely the magnitude of the particle size. For 23 catalysts samples of various particle sizes, only one minor discrepancy was observed. Some of the results are presented in Table 2; they give a good idea of the very close agreement between the physical methods for determining the metal particle size and the "chemical method" represented by the use of the selectivity in methylcyclopentane hydrogenolysis.

(6) The use of labeled hexanes shows that the isomerization of *n*-hexane to methylpentanes and vice-versa occurs more than 90% of the time according to a cyclic mechanism on any catalyst except on the ones with very large crystallites ($d_H >$ 150 Å). The results obtained by the Dutch workers, who used a catalyst with 80 Å particles are then very easily explained: with such a catalyst, one expects a cyclic mechanism of isomerization of *n*-hexane, with a nonselective ring opening of the cyclic intermediate; i.e., a ratio 2-methylpentane/3-methylpentane very close to 2.

(7) The interconversion between methylpentanes occurs according to a cyclic mechanism *only* for the very highly dispersed catalyst ($d <$ 50 Å). For the catalysts with a higher particle size, the bond shift mechanism is predominant.

All these results demonstrate clearly the existing correlation between the metal particle sizes and the various reaction routes in a catalytic reaction. As already outlined in our previous papers, we mean by particle size effect the influence of the size of the metal particles upon the formation of the various types of "defects" which are responsible for the various reaction mechanisms. In the case of supported metal catalysts, these defects appear during the early stage of the preparation of the reactive surface.

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Kinetics of Ethane Hydrogenolysis

The kinetics of the catalytic hydrogenolysis of ethane to methane have been investigated on all the Group VIII metals (*1*). A kinetic scheme originally proposed by Cimino *et al.* (*2*), extended to include situations in which adsorption equilibria are not established, was used for the interpretation of the results (*1*). The purpose of the present note is to reinterpret the kinetics in terms of a reaction sequence in which the step involving carbon–carbon bond scission has been revised. The new interpretation has the advantage of giving a much improved fit to the kinetic data, and leads to interesting conclusions regarding the chemisorbed hydrocarbon intermediates on the different metals. Two cases are considered, one involving equilibrium chemisorption of ethane and the other nonequilibrium chemisorption.

In the catalytic hydrogenolysis of ethane on metals, the available evidence indicates that ethane is chemisorbed with dissociation of carbon–hydrogen bonds (*1*). The resulting hydrogen-deficient surface species then undergoes carbon–carbon bond scission. Thus, the following sequence of reaction steps resulting in the formation of monocarbon surface fragments may be visualized:

$$C_2H_6 \overset{1}{\rightleftharpoons} C_2H_5(\text{ads}) + H(\text{ads}) \qquad (1)$$

$$C_2H_5(\text{ads}) + H(\text{ads}) \overset{2}{\rightleftharpoons} C_2H_x(\text{ads}) + aH_2 \qquad (2)$$

$$C_2H_x(\text{ads}) \overset{3}{\rightarrow} \text{adsorbed } C_1 \text{ fragments.} \qquad (3)$$

The symbol (ads) refers to an adsorbed species, and the quantity a is equal to $(6 - x)/2$. The initial chemisorption of ethane proceeds by dissociation of a carbon–hydrogen bond to form adsorbed C_2H_5. The latter then undergoes further rapid dehydrogenation to the species C_2H_x, such that equilibrium is essentially established between C_2H_5 and C_2H_x on the surface. The chemisorbed C_2H_x then undergoes carbon–carbon bond scission to yield monocarbon fragments which are rapidly hydrogenated to methane. The reaction scheme differs in one important respect from one that has been described previously (*1*), in that the step in which adsorbed C_2H_x undergoes carbon–carbon bond scission does not involve interaction of hydrogen with C_2H_x. This affects the kinetic analysis and conclusions regarding the composition of C_2H_x on most of the metals (*3, 4*).

If equilibrium is established in the overall chemisorption process, $C_2H_6 \rightleftharpoons C_2H_x(\text{ads}) + aH_2$, which is a combination of steps 1 and 2 of the reaction sequence, and if C_2H_x is the only surface species present in significant concentration, the fraction θ_x of the surface covered by C_2H_x may be represented by the expression:

$$\theta_x = (Kp_E/p_H{}^a)/(1 + Kp_E/p_H{}^a). \qquad (4)$$

Here K is an equilibrium constant, and p_E and p_H are the partial pressures of ethane and hydrogen, respectively. Over a restricted range of pressures, Eq. 4 can be approximated satisfactorily by the simpler relation:

$$\theta_x = (Kp_E/p_H{}^a)^n. \qquad (5)$$

The rate of hydrogenolysis corresponds to the rate of carbon–carbon bond scission to yield monocarbon fragments in step 3, which is characterized by a rate constant k_3. The rate is given by the expression

$$r = k_3\theta_x = k_3K^n(p_E/p_H{}^a)^n = kp_E{}^np_H{}^{(-na)}. \qquad (6)$$

The parameter k is equal to k_3K^n. The negative exponent $(-na)$ on hydrogen partial pressure is consistent with kinetic data on many metals. For a given metal the experimentally determined exponent n on ethane partial pressure can be used to determine the value of a which gives the best agreement between $(-na)$ and the experimental exponent m on hydrogen partial pressure. If permissible values of a are limited to integers from 1 to 3, corresponding to a variation of x in C_2H_x from 4 to 0, the "best fit" values summarized in Table 1 are obtained for a number of silica-supported Group VIII metal catalysts. In the kinetic analysis, the simplifying assumption was made that only one dehydrogenated surface species C_2H_x, rather than a distribution of such species with different values of x, need be considered for a given metal. It is emphasized that excellent agreement in Table 1 between the quantities m and $(-na)$ is obtained using integral values of a. A high value of a indicates a high probability that a primary dicarbon surface species will undergo further dehydrogenation as opposed to carbon–carbon scission. Interestingly, the metals with the highest value of a very likely have the highest ratios of dehydrogenation to hydrogenolysis activities. Thus, of the metals with a value of $a = 3$, platinum and palladium have by far the lowest hydrogenolysis activities (*1*). In the case of rhodium, the dehydrogenation activity

TABLE 1

KINETICS OF ETHANE HYDROGENOLYSIS: ANALYSIS OF HYDROGEN PRESSURE DEPENDENCIES

				Exponents in rate expression		
				Experimental[d]		Calculated[e]
Catalyst[a]	Temp. (°C)	x[b]	a[c]	Ethane (n)	Hydrogen (m)	Hydrogen ($-na$)
Co	219	4	1	1.0	−0.8	−1.0
Ni	177	2	2	1.0	−2.4	−2.0
Ru	188	2	2	0.8	−1.3	−1.6
Rh	214	0	3	0.8	−2.2	−2.4
Pd	354	0	3	0.9	−2.5	−2.7
Os	152	2	2	0.6	−1.2	−1.2
Ir	210	2	2	0.7	−1.6	−1.4
Pt	357	0	3	0.9	−2.5	−2.7

[a] All metals supported on silica.

[b] Specifies the composition of the surface species C_2H_x.

[c] Defined by the expression, $a = (6 - x)/2$.

[d] Exponents in the experimental power rate law, $r = kp_E{}^n p_H{}^m$ (*1*).

[e] Based on Eq. 6 in the text.

is probably unusually high, on the basis of its very high activity relative to other metals for hydrogenation (*5–7*) and ethane–deuterium exchange (*8*).

The kinetic analysis leading to Eq. 6 is not applicable to silica-supported iron or rhenium catalysts, for which the exponent on hydrogen partial pressure in the experimental power rate law is positive (*1*). In these cases the rate of ethane hydrogenolysis may be determined by the hydrogenation–desorption of monocarbon fragments, rather than carbon–carbon bond scission (*9*).

The derivation of Eq. 6 incorporates the simplifying assumption that competition between hydrogen and hydrocarbon for surface sites is insignificant. If such an effect were significant, it would alter the detailed form of Eq. 6 and could affect conclusions about the composition of the surface species C_2H_x (*3*, *4*). In any case, the simple kinetic analysis reveals an interesting trend in the variation of the composition of C_2H_x from metal to metal.

The assumption of adsorption equilibrium between ethane and the surface species C_2H_x, on which Eq. 6 is based, would appear to be satisfactory at the lower temperatures at which hydrogenolysis occurs. However, as the temperature is increased over a sufficiently wide range, the assumption of adsorption equilibrium eventually breaks down. In the case of a nickel catalyst, this is indicated by the result that the rate of exchange of ethane with deuterium becomes small compared to the rate of hydrogenolysis at sufficiently high temperatures (*10*). To account for the kinetics over a wide temperature range, it is necessary to modify the kinetic analysis. Referring to the sequence of reaction steps 1–3, we adopt a steady-state treatment in which the net rate of chemisorption of ethane in step 1 is just balanced by the rate of disappearance of C_2H_x via step 3. Assuming low surface coverage by all adsorbed species, we can write the equation:

$$k_1 p_E - k'_1 \theta_E \theta_H = k_3 \theta_x, \qquad (7)$$

where k_1 and k'_1 are the forward and reverse rate constants for step 1, and k_3 is the rate constant for step 3. The symbols θ_E, θ_H, and θ_x represent the fractions of the surface covered by C_2H_5, H, and C_2H_x, respectively, and p_E is the ethane partial pressure. Assuming that equilibrium is effectively maintained between adsorbed C_2H_5 and adsorbed C_2H_x in step 2, we can write the equilibrium relation:

$$K_2\theta_E\theta_H = \theta_x p_H{}^a, \qquad (8)$$

where K_2 is an equilibrium constant and p_H is the hydrogen partial pressure. The rate of hydrogenolysis is simply the rate of step 3, and is given by the expression:

$$r = k_3\theta_x. \qquad (9)$$

Combining Eqs. 7, 8, and 9, we obtain the rate equation:

$$r = k_1p_E/(1 + bp_H{}^a), \qquad (10)$$

where $b = k'_1/k_3K_2$. This analysis differs from a previously published one (*1*), since step 3 of the reaction sequence does not involve hydrogen as a reactant. Since the parameter b is temperature dependent, the dependence of the rate on hydrogen pressure is a function of temperature. If b decreases with increasing temperature, as found for cobalt (*1*, *11*), the rate equation at a sufficiently high temperature becomes simply, $r = k_1p_E$. This corresponds to the situation in which the chemisorption of ethane is completely irreversible. Under such conditions, step 2 of the reaction sequence may also become irreversible, so that the overall reaction may be considered simply as a sequence of irreversible steps. On the other hand, at a sufficiently low temperature, the term $bp_H{}^a$ in Eq. 10 becomes large compared to unity, and the rate equation becomes:

$$r = k_1p_E/bp_H{}^a = k_3K_1K_2p_E/p_H{}^a, \qquad (11)$$

where K_1 is the equilibrium constant of step 1 of the reaction sequence. Equation 11 corresponds to adsorption equilibrium being established between C_2H_6 and adsorbed C_2H_x, and is equivalent to Eq. 6 for $n = 1$. The equilibrium constant K in Eqs. 4–6 is equal to the product of K_1 and K_2.

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Some Remarks on the Activation Energy Variation in the Methanol Decomposition on Zinc Oxide

The kinetics of the methanol decomposition on zinc oxide has been investigated early by Dohse (*1*), who remarked on the Arrhenius plot a variation in the activation energy. That has been attributed to the consecutive steps:

$$CH_3OH \underset{(I)}{\rightarrow} CH_2O + H_2 \underset{(II)}{\rightarrow} CO + 2H_2,$$

with activation energies of ~20 and ~40 kcal $mole^{-1}$, respectively; the step (I) has been assumed as rate-limiting at higher and the step (II) at lower temperatures.