

Mechanism of the Hydrogenation of Ethylene on Pure Zinc Oxide

Poisoning Effect of Ethylene

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Kinetic studies of the hydrogenation of ethylene on zinc oxide have demonstrated the occurrence of a poisoning effect which induces catalyst heterogeneity in addition to the initial heterogeneity. Ethylene gives an irreversibly adsorbed poison whose presence can be overlooked to some extent only with hydrogen-rich mixtures. The increase of the reaction temperature modifies the surface heterogeneity. A kinetic reaction mechanism is proposed which takes into account these phenomena. It is concluded that under such conditions no collective properties can be correlated to the catalytic activity. These conclusions are common to a catalyst prepared at low temperature or high temperature, pure or doped.

I. INTRODUCTION

Hydrogenation of ethylene over metals has been extensively studied (1, 2) but investigations concerning metal oxides as catalysts are rather scarce, most of them dealing with activity patterns and some concerning kinetic studies. One attempt was recently made to correlate catalytic activity and the *d*-character of these solids (3).

The activity of ZnO was compared with its electronic properties by one of us (4, 5) and it was shown that only the nonstoichiometric oxide is active at 150°C. Nevertheless, results obtained with lithium- or gallium-doped samples gave no evidence of any electronic transfer being the rate-controlling step.

These results require extension of the investigation in different directions. The

intention of this paper is to give further information on the nature of the interaction of reagents (Langmuir or Rideal-Eley mechanism, inhibition steps). Consequently the temperature and pressure ranges of the reaction are extended (80° to 400°C) and the kinetic results are contrasted with infrared data concerning adsorbed species (6).

A comparison of pure and doped samples, prepared either at low or at high temperatures, with regards to their structure, electronic properties, and catalytic activity, must also be attempted to cast some light on the uncertainties concerning the modification of the electronic structure of an oxide through doping (7). This comparison is presented elsewhere (8, 9).

This paper deals with pure zinc oxide prepared at different temperatures. Indeed, an increase in the preparation temperature of the catalyst may induce a modification of its surface structure, sensitive enough to change the reaction pattern. For in-

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stance, in the case of the nickel oxide, an increase of only 50°C in this temperature changes the mechanism of the catalytic oxidation of CO (10).

II. EXPERIMENTAL

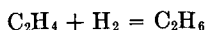
1. Catalysts

Zinc hydroxide (11) was the starting material for all catalysts used. The ZnO L.T. (low-temperature) sample was prepared by decomposition of the zinc hydroxide *in vacuo* at 120°C (2 hr) and then, activation *in vacuo* (10^{-6} torr) at 400°C (12 hr).

The ZnO H.T. (high-temperature) sample was prepared by decomposition of the hydroxide at 850°C in air (12 hr) and then, activation *in vacuo* (10^{-6} torr) at 450°C (36 hr).

2. Apparatus

The rate of the hydrogenation of ethylene



was followed by the pressure change in a constant volume reaction vessel provided with a circulation pump. The experimental procedures for the electrical conductivity measurements (12) and infrared spectroscopy of the adsorbed species (6) were reported previously.

III. HYDROGENATION OF ETHYLENE OVER ZnO L.T.

The runs were performed over samples of 467 mg (5.9 m^2). In the following discussion the partial pressures of hydrogen and ethylene are denoted as p_{H} and p_{E} .

1. Activation of the Catalyst

The data listed in the Table 1 show that the catalytic activity increases with the activation temperature despite a decrease of the surface area.

The electrical conductivity, measured at 150°C, does not change very much with the activation temperature in the 250–500°C range (1.0×10^{-2} to $3.5 \times 10^{-2} \text{ ohm}^{-1}\text{cm}^{-1}$). Mass spectrographic analysis shows that the sample evolves water even

after activation at 500°C but no experimental evidence is found concerning the hydroxyl content of the surface, which is probably already on the lowest level after a treatment at 300°C as shown by the weight loss. By analogy with the work

TABLE 1
SURFACE AREA AND ACTIVITY VS. THE
ACTIVATION TEMPERATURE

Activation temperature (°C)	Surface area (m^2/g)	Reaction half-life ($t_{1/2}$)
120°	32.5	> 8 hr
250°	31.8	> 8 hr
300°	18.6	> 8 hr
350°	15.3	> 8 hr
400°	12.5	45 min
500°	8.5	35 min

carried out on the decomposition of nickel hydroxide to give nickel oxide catalyst (7) it is supposed that the activation temperature of zinc oxide modifies its chemical defect structure (anionic and cationic vacancies, interstitial atoms) and induces a variation of its surface energy spectrum.

2. Poisoning and Regeneration of the Catalyst

A series of experiments performed at 162°C have shown that a sample already used in a first run is less active than a fresh one.

The results listed in Table 2 concern successive experiments on the same sample, separated by an evacuation at 162°C under 10^{-6} torr.

TABLE 2
SUCCESSIVE EXPERIMENTS OVER ZnO L.T.

Sample	Reaction half-life $t_{1/2}$ (min)
Fresh	45
After 1st run	80
After 2nd run	100
After 3rd run	60

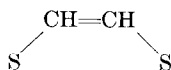
Furthermore the initial activity cannot be restored by a single outgassing even at 400°C. A complete regeneration of the

catalyst requires a treatment by oxygen (under 5 torr) at 400°C followed by an outgassing at this temperature. No change of the surface area is recorded after the regeneration. It appears therefore, that at the end of the reaction, the catalyst is partly covered by a strongly adsorbed poison.

A second series of runs indicates that ethylene is responsible for this poisoning. If indeed this reactant is previously adsorbed onto the catalyst at the reaction temperature (162°C), the initial reaction rate is only 0.10 torr/min, while it amounts to 1 torr/min for a fresh sample. On the other hand, pretreatment in hydrogen or ethane has no effect.

Infrared study of the species adsorbed on ZnO L.T. has shown (6) that ethylene chemisorption produces an absorption band at 1540 cm^{-1} , while its intensity increases when the adsorption temperature is raised from 80° to 200°C. This band is altered neither by a prolonged outgassing at the adsorption temperature, nor by hydrogenation at the same temperature. But if the catalyst had previously adsorbed hydrogen, the band does not appear. Woolman and Taylor (13) reported that at 210°C ethylene slowly polymerizes on ZnO, but this has not been observed in the present work, even at 400°C.

The structure of the poison was discussed in a previous paper and is assumed to have a vinylidenic form



where S designates an adsorption site.

The presence of this poison explains the failure in the attempts of regeneration by single outgassing. The oxidation procedure must transform the poison into CO_2 and H_2O which later are desorbed *in vacuo*.

A similar species was already mentioned by Beeck (14) and by Jenkins and Rideal (15) (called by these authors "acetylenic complex") to account for the observed kinetics of the hydrogenation of ethylene on nickel. As reported below, the kinetic

behavior of ZnO and nickel present remarkable analogies.

3. 80–125°C Range

At 80° and 100°C the overall reaction order amounts to 0.8, but between 110° and 125°C it increases to unity. At 112°C the reaction rate follows the law

$$v = k p_{\text{H}} \quad (1)$$

provided ethylene is not in excess in the reaction mixture. If this is not the case, the initial rate is smaller than expected and Eq. (1) is no longer valid. The apparent activation energy measured between 110° and 125°C with a stoichiometric mixture is 21 ± 2 kcal/mole.

4. 140–175°C Range

The partial orders were determined at 162°C.

Initial orders. The initial orders, that is the orders with respect to the initial pressures of hydrogen and ethylene, are 0.3 and 0.7, while the initial overall order is equal to unity. Therefore at time zero the kinetic law is

$$v_0 = k(p_{\text{H}})_0^{0.3}(p_{\text{E}})_0^{0.7} \quad (2)$$

Again these results are observed only for reaction mixtures with the ratio $(p_{\text{H}})_0/(p_{\text{E}})_0 \geq 1$. For ethylene-rich mixtures, the experimental data do not any longer fit Eq. (2). The initial rate decreases when $(p_{\text{E}})_0$ increases at constant $(p_{\text{H}})_0$.

Orders with respect to time. These orders are established as a function of the time-varying pressure. The variations of $\log v$ against $\log p/p_0$ (where $p = p_{\text{E}} = p_{\text{H}}$) plotted in Fig. 1 are not linear during the initial stage of the reaction. The slope (which represents the overall order with respect to time) is initially higher than 2, then it decreases and remains constant. The slope of the straight portion increases with p_0 (Table 3) and its value is, in any case, greater than the overall initial order (one). Clearly, a perturbing effect occurs during the reaction which raises the overall order to an apparent value higher than 1. An introduction of ethane (product of the

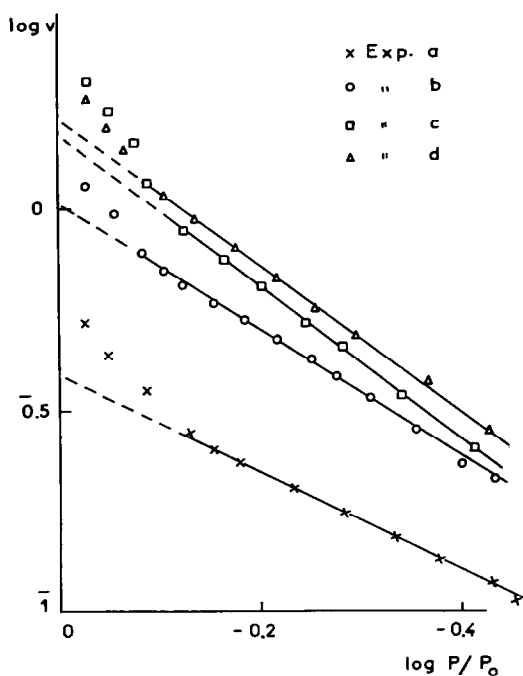


FIG. 1. Determination of the apparent overall order of reaction with respect to time at 162°C.

reaction) in the initial reaction mixtures does not change the reaction rate.

These data evidence therefore the occurrence of a poisoning phenomenon which cannot be ascribed but to ethylene, according to the results presented in Section 2.

The partial order with respect to ethylene, measured with hydrogen-rich mixtures, is close to 0.7 and therefore equals the initial order.

Unfortunately, the isolation method could not be applied in determining the order towards H_2 , because, with ethylene-rich mixtures the variations of $\log v$ against $\log p_H/(p_H)_0$ are no longer linear, the slope of the curve decreasing steadily as the reaction proceeds (Fig. 2). This slope is

TABLE 3
APPARENT OVERALL ORDER AT 162°C

Experiment	p_0 (torr)	Overall order
a	29.7	1.25
b	56.9	1.50
c	112.3	1.80
d	115.4	1.80

close to 3 at the beginning of the reaction, which accounts for a decrease of the active surface and must be ascribed to the poisoning phenomenon. The subsequent decrease of the slope value may be explained by a diminution of the poisoning rate.

The partial order with respect to hydrogen was therefore measured by the following procedure. Several reaction mixtures were used in which the ratio $(p_H)_0/(p_E)_0$

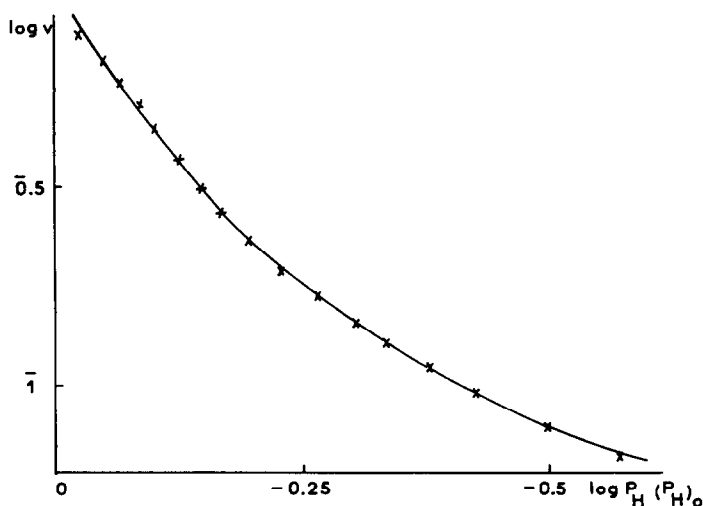


FIG. 2. Attempt to determine the order towards hydrogen with respect to time at 162°C, by the isolation method.

was in every case ≥ 1 , $(p_E)_0$ being kept constant. For a given p_E value, obtained after some reaction has proceeded, the reaction rate depends solely upon p_H . The slope of the mean straight line plotted in Fig. 3 represents this order. Although this

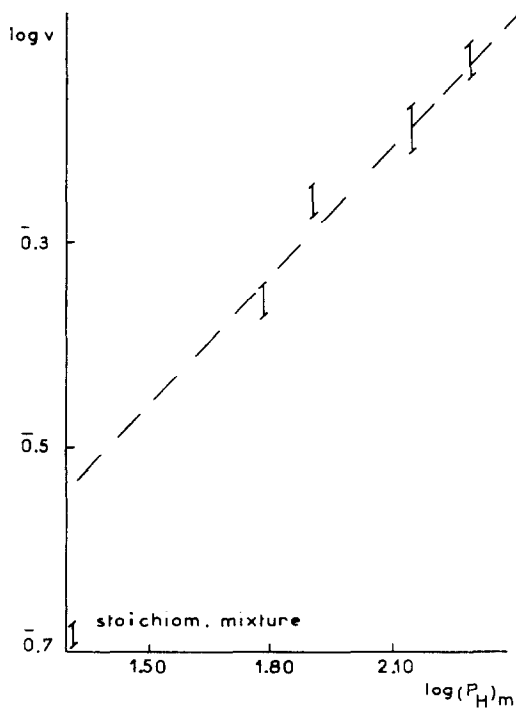


FIG. 3. Determination of the order towards hydrogen with respect to time at 162°C.

procedure is not precise, it allows the following conclusions to be drawn: The order towards hydrogen (with respect to time) amounts to 0.4 ± 0.15 . This value is observed only with hydrogen-rich mixtures because the experimental points obtained with stoichiometric mixtures do not coincide with the straight line of Fig. 3.

It therefore appears that for hydrogen-rich mixtures, the reaction order with respect to time nearly equals the initial order, that is the kinetic law may be written

$$v = kp_H^{0.3}p_E^{0.7} \quad (2a)$$

Finally, the apparent activation energy, measured from the initial rate (time zero, nonpoisoned surface) is found to be rather

low (4.5 ± 1 kcal/mole) in the range 145–175°C (initial order of unity). The Arrhenius plot for the 1.5 order rate constants ($p_0 = 56.9$ torr) gives an activation energy of 6 ± 0.5 kcal/mole.

5. Kinetics at 210°C

Data from Table 4 show that the initial partial order is zero with respect to hydrogen and 1 with respect to ethylene, provided ethylene is not in excess in the reaction mixture. The same values are found for the orders with respect to time, except for the experiment (f) with an ethylene-rich mixture.

If therefore the ratio $(p_H)_0/(p_E)_0$ is ≥ 1 , the reaction rate follows the law

$$v = kp_E \quad (3)$$

The partial order with respect to hydrogen, measured during experiment f is close to 1.2 but this value must be considered as an apparent one. Indeed, the following results show that a decrease of the active surface, due to an excess of ethylene, proceeds during the run f.

TABLE 4
INITIAL RATES AT 210°C

Experiment	$(p_H)_0$ (torr)	$(p_E)_0$ (torr)	v_0 (torr/min)
a	62.3	62.3	2.08
b	59.8	59.8	1.90
c	125.4	62.7	1.82
d	192.6	64.2	2.15
e	104.2	104.2	3.20
f	65.0	130.0	2.26

After the run e, the catalyst was out-gassed for 15 min at 210°C and a second run was performed. The initial rate was decreased by 20%. The same procedure was followed with run f and the observed decrease was 60%, which means that the ethylene-rich mixture is much more deactivating than a stoichiometric one.

Moreover, if ethylene is introduced onto a fresh sample t_E min before hydrogen and under the same pressure, the initial rate decreases as t_E increases (Table 5).

The reaction rate still follows the first

TABLE 5
INFLUENCE OF THE PREADSORPTION OF
ETHYLENE ON THE INITIAL RATE
OF THE REACTION

t_E (min)	v_0 (torr/min)	k (min ⁻¹)
0	2.0	3.3×10^{-2}
1.5	0.50	1.1×10^{-2}
3	0.41	8.0×10^{-3}
15	0.36	7.0×10^{-3}
60	0.33	5.9×10^{-3}

order law but the rate constant k decreases with increasing t_E . It is therefore concluded that ethylene-rich mixtures partly deactivate the catalyst as does preadsorbed ethylene.

6. Kinetics above 210°C

At 225°C the overall reaction order is still unity but the initial rate and the rate constant are lower than those registered at 210°C. This means that the Arrhenius plot exhibits a maximum near 210°C (Fig. 4) which may be ascribed to the desorption

of the oxide surface and probably increases the concentration of surface Zn⁺ ions (5, 6) but not their conversion into Zn atoms.

Above 300°C the reduction of the catalyst is too drastic to allow any interpretation of the kinetic results. Degeneracy to a metallic state is specially noticeable at 400°C (6). At this temperature the overall order is still one, but for hydrogen-rich mixtures a zinc film appears on the cold walls of the reactor. Metallic zinc is not a catalyst of the hydrogenation of ethylene (16) and the decrease of the initial hydrogenation rate with the increase of the reaction temperature may be ascribed to the degeneracy of the catalyst.

7. Reaction Mechanism

Previous results show that the reaction of ethylene-rich mixtures never follows the same law as other mixtures do. Furthermore, at 162°C, the true reaction order can only be determined with hydrogen-rich mixtures. The data reported in Section

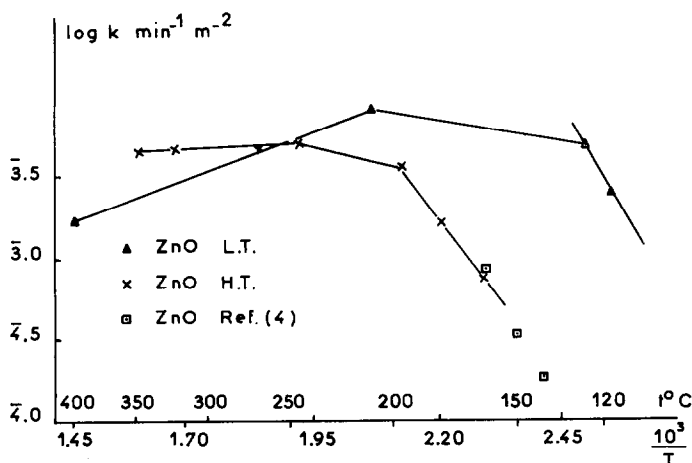


FIG. 4. Arrhenius plot for zinc oxide samples.

of ethylene (see below). At 250° and 300°C the overall reaction order approaches zero, a value which is accounted for by the catalyst activation by hydrogen during the reaction. In this way, the first order rate decrease is balanced by an increase of the activity. This activation involves a partial reduction, without degeneracy,

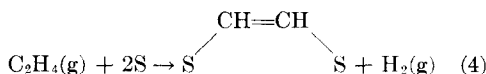
2 cast some light on these anomalies and any explanation must involve a surface poisoning by ethylene.

An ethylene poisoning effect has been already reported for nickel catalysts (14, 15). In addition, chemisorption of ethylene over nickel produces species which are inactive towards hydrogen as shown by

using ^{14}C -labeled ethylene (17). The decrease of the initial rate observed when increasing the ratio $(p_E)_0/(p_H)_0$ was ascribed to an "irreversible poisoning effect" (18).

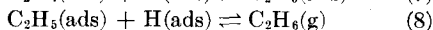
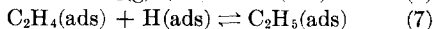
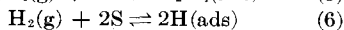
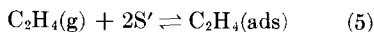
Similarly, the surface of a copper catalyst is irreversibly deactivated during the reaction (19) which was called later a "memory effect" (20).

The catalytic behavior of ZnO may then be explained by considering that the poison cannot be converted into ethane. Therefore, ethylene must simultaneously act as a reactant and be transformed into a poison. The surface concentration of the poison must be high for ethylene-rich mixtures and low for hydrogen-rich mixtures. This is accounted for by the following poisoning scheme (see Section 2):



As the preadsorption of hydrogen prohibits the formation of the poison, it is concluded that hydrogen and poison compete for the same kind of sites (S), which discards the Rideal mechanism involving gaseous hydrogen. On the other hand the hypothesis of the Rideal mechanism involving gaseous ethylene does not conform with the results as shown below.

According to the infrared data, hydrogen must be adsorbed as an atom (21) and the ethylene adsorption should be of the associative type (6). The following mechanism accounts for the kinetic data in the 110–300°C range:



As the adsorption of the poison is drastically irreversible, the poisoning phenomenon cannot be described by a classical equilibrium treatment. In the following discussion θ_H and θ_p are denoted as the fraction of S sites covered by hydrogen and poison respectively, while θ_E is the fraction of S' sites covered by active ethylene. θ_p

is a rising function of time. At equilibrium, which concerns only θ_H and θ_E (on the unspoiled part of the surface), these quantities may be written.

$$\theta_E = \frac{b_E p_E}{1 + b_E p_E} \quad (9)$$

$$\theta_H = \frac{b_H^{1/2} p_H^{1/2} (1 - \theta_p)}{1 + b_H^{1/2} p_H^{1/2}} \quad (10)$$

where b_H and b_E are adsorption coefficients.

110–125°C range. The kinetic data can be explained only if the rate-controlling step is (6) or (8). However the high value of E_a (21 ± 2 kcal/mole), much higher than the activation energy of adsorption of hydrogen (22), favors the second hypothesis. Neglecting θ_p , the rate law derived from Eqs. (8), (9), and (10) may be written (Langmuir-Hinshelwood mechanism)

$$v = \frac{k b_H p_H}{(1 + b_H^{1/2} p_H^{1/2})^2} \frac{b_E p_E}{1 + b_E p_E} \quad (11)$$

If hydrogen is weakly adsorbed while ethylene fully covers its sites, (11) is reduced to the experimental equation (1). For ethylene-rich mixtures θ_p cannot be neglected and it accounts for the abnormally low initial rate.

140–175°C range. The rate-controlling step may be either (7) or (8), the calculated rate laws being very similar. If Eq. (8) represents again the slowest step, the rate equation is given by

$$v = \frac{k b_H p_H b_E p_E (1 - \theta_p)^2}{(1 + b_H^{1/2} p_H^{1/2})^2 (1 + b_E p_E)} \quad (12)$$

(i) For hydrogen-rich mixtures, θ_p can be held as $\ll 1$ and (12) is reduced to (11) which agrees with the experimental law Eq. (2a).

(ii) For stoichiometric mixtures, θ_p is likely to be weak during the earlier stages, and Eq. (11) accounts only for results recorded at time zero [Eq. (2)].

But θ_p increases when the reaction is proceeding and only Eq. (12) fits in with the results. Introducing $p = p_H = p_E$, the logarithmic form of (12) may be written

$$\log v = f(\log p/p_0) + 2 \log (1 - \theta_p) \quad (13)$$

Therefore the apparent overall reaction order depends upon the variations of $(1 - \theta_p)$ with time. The second term of the right-hand member is initially close to zero but then becomes more and more negative. The decrease of the rate proceeding from this term adds to the first order decrease, which causes the apparent overall order to be greater than the true order.

(iii) For ethylene-rich mixtures, Eq. (12) explains the data obtained throughout the reaction. Hydrogen pressure being the only variable, the logarithmic transformation of (12) yields

$$\log v = f \log p_{\text{H}}/(p_{\text{H}})_0 + 2 \log (1 - \theta_p) \quad (14)$$

This expression accounts for the impossibility of measuring the true order with respect to hydrogen by the isolation method (Fig. 2).

210–300°C range. The occurrence of a maximum in the Arrhenius plot (Fig. 4) is another kinetic feature, well observed for metal catalysts (nickel, palladium, plat-

hydrogen fully covers S sites, Eq. (12) rearranges to

$$v = kp_{\text{E}}(1 - \theta_p)^2$$

which accounts for the value 1.2 of the apparent order with respect to hydrogen for an ethylene-rich mixture and fits the experimental law (3) for stoichiometric and hydrogen-rich mixtures ($\theta_p \ll 1$).

8. Variation of the Kinetic Parameters between 80° and 225°C

It appears from the data listed in Table 6 that the steep decrease of E_a in the 110–225°C range does not necessarily involve a change of the reaction mechanism (23). This interpretation requires only that the heat of adsorption Q_{H} is $\ll Q_{\text{E}}$, which is a reasonable assumption considering the poisoning phenomenon. In this way, the decrease of the reaction order with respect to hydrogen must correspond to an increase of the surface coverage by this reagent. This behavior is not surprising as many

TABLE 6
ACTIVATION ENERGY AS A FUNCTION OF REACTION ORDER^a

Temperature range (°C)	Reaction order towards		Coverage		E_a (kcal/mole)	Expression for E_a
	H ₂	C ₂ H ₄	θ_{H}	θ_{E}		
110–125°	1	0	$\ll 1$	1	21 ± 2	$E_v - Q_{\text{H}}$
140–175°	0.3	0.7	~ 0.5	~ 0.5	4.5 ± 1	$E_v - \lambda_{\text{H}}Q_{\text{H}} - \lambda_{\text{E}}Q_{\text{E}}$
210–225°	0	1	1	$\ll 1$	< 0	$E_v - Q_{\text{E}}$

^a λ_{H} and λ_{E} are coefficients < 1 ; E_a , apparent activation energy; E_v , true activation energy.

inum). The experimental data reported at 210°C might be explained by the Rideal mechanism involving gaseous ethylene but this assumption does not explain negative values of the apparent activation energy. On the other hand, assuming the Langmuir mechanism, these values can be accounted for by the desorption of ethylene which implies that the heat of adsorption of ethylene is greater than the true activation energy (23). The situation is summarized in Table 6.

Indeed, the partial order with respect to C₂H₄ increases from zero to one between 110° and 225°C. Assuming that S' sites are scarcely covered by ethylene and that

data emphasize the heterogeneous character of zinc oxide with respect to hydrogen. For instance, the variation of the amount of hydrogen adsorbed on ZnO, deduced by Cimino *et al.* from adsorption isobars (24) is very much like the variation of θ_{H} presented in Table 6. The decrease of the coverage by ethylene (the active form) when the temperature increases, is in agreement with the infrared observation of an increased formation of vinylidene species (the inactive form of ethylene) as the temperature rises.

From this observation it may be seen that any correlations between the catalytic activity and the electronic structure may

be obscured by the initial surface heterogeneity of the catalyst still enhanced by the heterogeneity induced by poisoning. Careful kinetic examinations, and not only a single determination of the activation energy of the reaction by simplified procedures, are necessary to deduce or to eliminate any correlation between the activity and some collective properties. In the present case this type of correlation is not to be expected because of the initial and induced heterogeneity. It is obvious that the energy spectrum of the surface sites may still be modified by a change in the preparation temperature of the oxide and also by doping (7, 10).

IV. HYDROGENATION OF ETHYLENE OVER ZnO H.T.

The experiments were performed over 1 g of the ZnO H.T. sample (3.9 m²). The sample was first heated in air at 850°C, and then cooled down to room temperature, and finally activated *in vacuo* at 450°C. The cooling rate was shown to have some influence on the catalytic activity, which was also increased by the duration of the activation procedure. This was not observed for ZnO L.T. and may probably be ascribed to a slower diffusion of Zn⁺ ions towards the surface in the sintered sample (12).

The results obtained over the whole 162–350°C range are listed in Table 7. In addition, partial orders were determined at 162° and 325°C.

At 162°C the kinetics conforms to the first order law with respect to hydrogen, whereas at 325°C it obeys the first order

law with respect to ethylene. With hydrogen-rich mixtures precautions must be taken as the catalysts undergo an extra activation during the reaction.

Over the whole studied range the overall order remains equal to unity. The apparent activation energy E_a steadily decreases to a zero value above 250°C.

Thus the kinetics over ZnO H.T. appears to parallel roughly the kinetics over ZnO L.T. (Tables 6 and 7). It is nevertheless shown in Fig. 4 that the Arrhenius plot relative to ZnO H.T. is shifted by about 50°C towards the higher temperatures. In the same figure (where the rate constants

TABLE 8
ELECTRIC PROPERTIES OF PURE ZnO

Sample	Conductivity at 150°C under vacuo (ohm cm) ⁻¹	Activation energy of conductivity between 150° and 250°C (kcal/mole)
ZnO L.T. (this work)	3.0×10^{-2}	1.2
ZnO L.T. (previous work)	1.6×10^{-2}	1.51
ZnO H.T.	1.3×10^{-2}	1.75

are calculated per unit surface area) are also reported the previous results obtained by one of us (4) with another L.T. sample [decomposition of Zn(OH)₂ at 250°C]. They perfectly conform with the H.T. sample studied in this work. The electric properties of these three samples are compared in Table 8.

One would be tempted to correlate the shift in the activity of the ZnO H.T.,

TABLE 7
ACTIVITY OF THE ZnO H.T. SAMPLE IN THE RANGE 162–350°C

Temperature of reaction (°C)	Overall order	Initial rate (torr/min)	Rate constant (min ⁻¹)	Apparent activation energy (kcal/mole)
162°	1	0.19	2.4×10^{-3}	17
177°	1	0.30	4.9×10^{-3}	
196°	1	0.68	1.0×10^{-2}	
248°	1	1.27	1.5×10^{-2}	4
269°	1	1.11	1.4×10^{-2}	
325°	1	1.36	1.6×10^{-2}	0
350°	1	1.33	1.6×10^{-2}	

compared to the ZnO L.T. (Fig. 4) with some difference in the electron concentration of these solids. As the electric properties for all catalysts are very similar (Table 8), the differences in the catalytic activity should be correlated with some local surface properties instead of the collective ones.

V. CONCLUSIONS

The results described here emphasize the significance of a poisoning effect involving ethylene during the hydrogenation of this olefin over zinc oxide. This effect, which is quite irreversible, cannot be described by a classical equilibrium treatment. It tends to increase the apparent reaction order with respect to time, the autoinhibition proceeding from the conversion of ethylene into an inactive species.

This autoinhibition by a reactant makes uneasy any determination of the activation energy. For instance, in the case of the ZnO L.T. sample one value of the activation energy, in the range 140–175°C, is determined from the initial rate. Indeed, the initial overall order is 1, while the overall order with respect to time has an apparent value, higher than 1, due to poisoning by ethylene. The inhibiting action of ethylene may be reduced to some extent for hydrogen-rich mixtures, but it can never be ascertained that the poisoning effect for any mixture operates with the same intensity over the whole temperature range of Fig. 4. Infrared results and the kinetic determinations in the range 80–160°C show that poisoning is increased when the temperature increases.

Careful kinetic determinations are therefore required, instead of a simplified calculation of the activation energy, to stress that the initial surface heterogeneity still may be changed by poisoning and may vary with temperature, ruling out any correlations which one would be tempted to establish when considering the values of the activation energy alone. Kinetic equations developed in this work, which depend upon the temperature range and the nature of the mixture imply that some local prop-

erties vary with the nature of the mixture, the temperature, and the course of the reaction itself. Any correlation between the catalytic activity and some collective properties is therefore ruled out.

But this behavior is not found only for a catalyst prepared at low temperature. Indeed, one would be inclined to suppose that the heterogeneity of the catalyst (initial and induced) may be very much reduced by increasing the preparation temperature of the zinc oxide. The parallel behavior of the sample prepared at high temperature shows that despite some modification of the surface properties, the surface heterogeneity must again be considered. Therefore doping by altermultivalent ions, even at high temperature (9), would not give a homogeneous surface but rather would change to a still higher extent the energy spectrum of the surface sites (7, 10), enhancing again the influence of local properties upon the catalytic activity.

A careful examination of the kinetics of the reaction over the whole temperature range should be carried out again for doped catalysts, and one should not only proceed to a simple comparison of some values of the activation energy of the reaction with the intensity and the nature of doping. The energy spectrum of an heterogeneous surface (initially and by induction) may be the determining factor in the catalytic activity which becomes difficult to relate to some collective properties.

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