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The Hydrogenation of Ethylene on Zinc Oxide Catalysts

JEAN AIGUEPERSE AND STANISLAS JEAN TEICHNER

From the University of Lyon, Faculté des Sciences, Institut de Recherches sur la Catalyse, Villeurbanne, France

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The kinetic study of the hydrogenation of ethylene in the presence of zinc oxide shows that the rate of the reaction is proportional to the partial pressure of hydrogen, provided that an excess of ethylene in the reaction mixture is avoided. Neither the rate constant nor the activation energy of the reaction are varied when the zinc oxide contains lithium or gallium ions modifying its electronic structure.

INTRODUCTION

The correlations between the catalytic activity of semiconducting oxides and their electronic structure do not seem to have any predictive value. These discrepancies were clearly analyzed by Boudart in a recent paper (*1*). It should be noted on this subject that the surface activity of a catalyst should be modified by a mere surface modification of the electronic structure of the solid. This surface modification is usually carried out by the substitution of altervalent ions in the bulk of the solid by a high-temperature treatment. However the same result should be reached at a much lower temperature if the substitution is desired to be carried only on the surface layer of the catalyst. In this case the catalyst preparation bears some resemblance to the elaboration of industrial catalysts in which temperatures giving rise to sintering are avoided.

The electronic properties of pure zinc oxide and of oxides doped at low temperatures with lithium or gallium were extensively studied by one of the authors (*2*). The chemisorption of hydrogen by zinc oxide has been studied for many years and information is available on the nature of chemisorption of hydrogen at different temperatures (*2, 3*). The adsorption of ethylene by pure and doped zinc oxides was also studied by one of the authors (*2*). For these reasons we thought it was worthwhile to start the study of the hydrogenation of ethylene on pure zinc oxide and on oxides containing Li^+ or Ga^{3+} ions, whose presence modifies the electronic structure of the solid.

METHODS

The pure zinc oxide is prepared by decomposition of the zinc hydroxide *in vacuo* at 110°C (*4*). It is then activated *in vacuo* at 250°C. Doping with LiOH or $Ga(OH)_3$ is principally carried out by heating the mixture of hydroxides *in vacuo* at 250°C (*5*). The surface area of pure zinc oxide and of doped oxides after heating to 250°C is the same (31 m^2/g). The amount of lithium or gallium is calculated so as to have an altervalent ion for every zinc ion on the surface of the zinc oxide. The electric conductivity studies of the samples show that this method of doping is efficient (*2*) and no improvement is observed by heating up to 400°C, whereas the surface area of the catalysts decreases to 10 m^2/g. The hydrogenation of ethylene is carried out in a constant volume system equipped with a circulating pump. The amount of reaction is followed by the pressure changes measured with a mercury manometer.

RESULTS AND DISCUSSION

Hydrogenation of Ethylene by Pure Zinc Oxide

The theoretical discussion of this reaction in the light of the mechanism of Langmuir-

Hinshelwood or the mechanism of Rideal was given in a previous paper (*5*).

To exhibit catalytic activity at 150°C zinc oxide must be activated *in vacuo* (10^{-6} mm Hg) at a minimum temperature of 250°C, for 12 hr. In each experiment of hydrogenation a fresh catalyst was used, as the reproducibility of the results was excellent with these conditions. The amount of catalyst in the system was always 700 mg, which represented a surface of 22 m^2. The analysis of the products of the reaction showed that the decrease of pressure was in agreement with the equation:

$$C_2H_4(g) + H_2(g) = C_2H_6(g)$$

Table 1 gives the initial partial pressures of the reagents and the initial rate recorded. The decrease of the total pressure with time is shown in Fig. 1. With the exception of mixture No. 6, which contains an excess of ethylene, the initial rate is proportional only to the partial pressure of hydrogen. The initial partial order of reaction with respect to hydrogen is then one. The logarithms of the instantaneous rates of the reaction ($-dP/dt$) plotted as a function of time (Fig. 2) follow a straight line and give evidence that, except for mixture No. 6 when the rate is constant (order zero) the total order of reaction with respect to time remains one. If this order depends on the partial pressure of hydrogen only, then all the mixtures (No. 6 excepted) should give the same straight line passing through the origin of ordinates whatever the initial total pressure of P_0, if they are plotted as:

$$\log p_H/(p_H)_0 = -(0.4343k)t = -k't$$

TABLE 1
REACTION RATES

No.	p_{H0} (mm Hg)	p_{E0} (mm Hg)	Initial rate at 150°C (mm Hg/min)
1	26.5	26.5	0.16
2	51.5	51.5	0.32
3	60.0	60.0	0.37
4	102.2	51.5	0.67
5	102.7	102.7	0.64
6	51.7	103.4	0.09

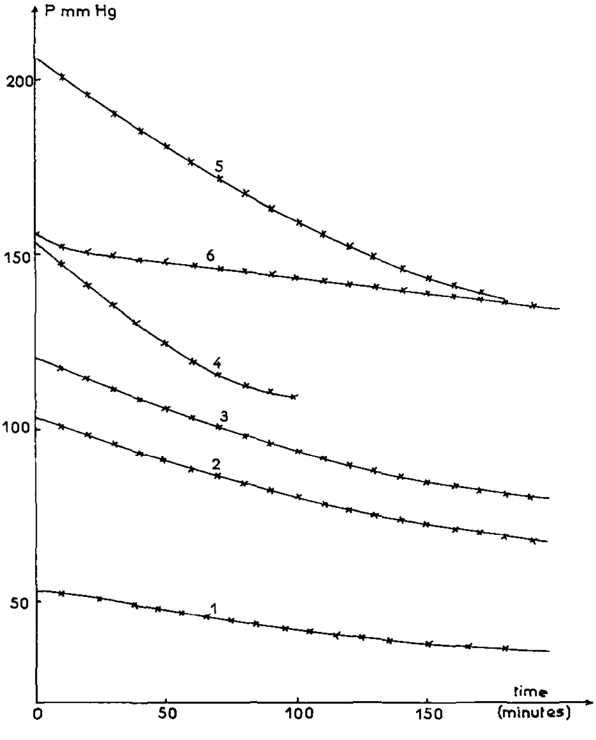

FIG. 1. Experimental kinetics for mixtures of Table 1.

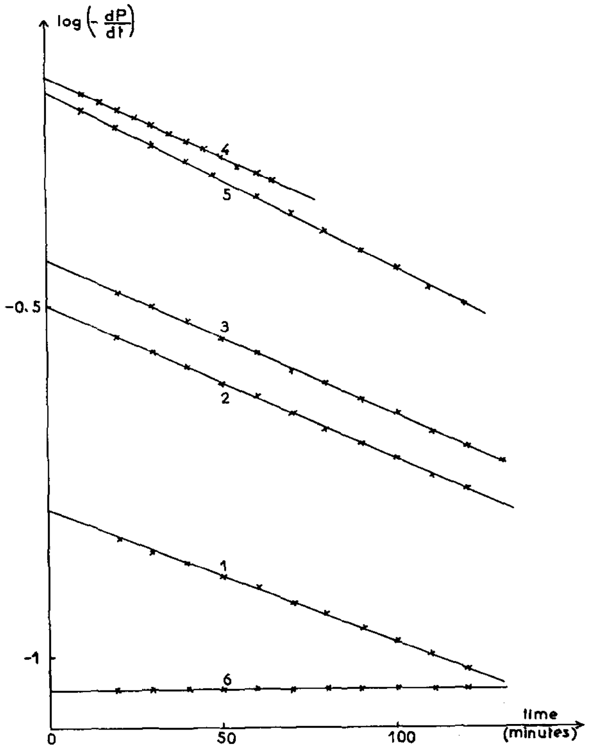

FIG. 2. Logarithmic plot of reaction.

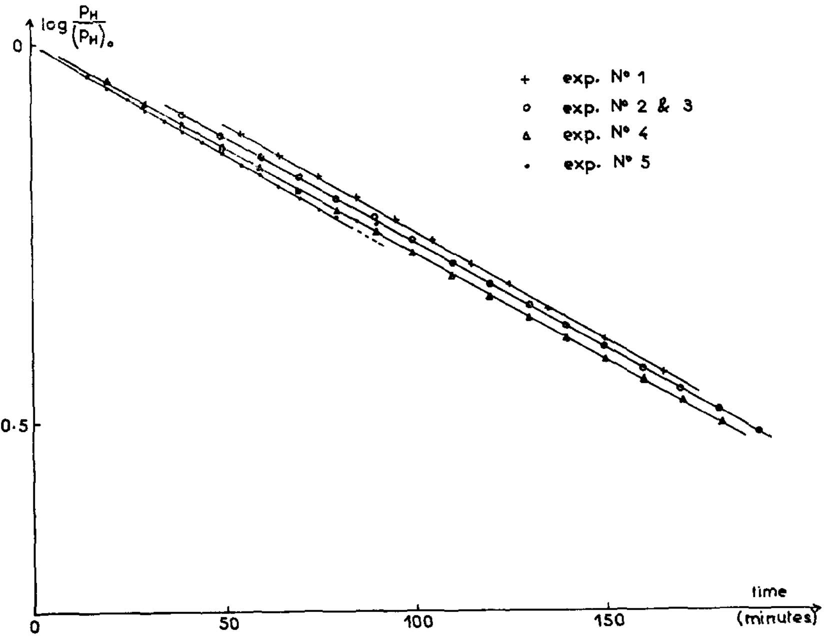

FIG. 3. First order plot of kinetic results.

where p_H is the partial pressure of hydrogen and $(p_H)_0$ is this pressure at time zero. The slope of this line represents the rate constant of the reaction.

The straight lines of Fig. 3 which exhibit the same slope and are very close together show that this hypothesis is correct. The rate constant does not depend on the initial pressure of hydrogen and represents the specific rate, as the amount of catalyst and its surface area are constant for all the experiments.

An examination of the kinetic data in terms of Langmuir kinetics discloses that hydrogen and ethylene must be adsorbed on two kinds of sites, the hydrogen adsorption being weak and the Rideal mechanism being discarded for reasons given in ref. (*5*). A strong adsorption of two reagents on such a surface would give zero order and a weak adsorption would give order two. The hypothesis that hydrogen and ethylene are adsorbed and compete for the same surface, regarded as uniform, must be discarded as it does not lead to the order one of reaction.

The kinetics for mixture No. 6 corresponds to an order zero, up to 60% of the reaction. There are many examples in the literature giving evidence that an excess of ethylene strongly decreases the rate of the reaction (*6*). As the adsorption of hydrogen cannot be strong when an excess of ethylene is present, the zero order must result from the increase with time, up to equilibrium value, of the adsorption coefficient of hydrogen in a mixture containing an excess of ethylene. A compensation between the decrease of the hydrogen pressure with time and the increase of its adsorption coefficient may result in a constant rate for some amount of the reaction.

The rate constants determined between 140° and 160°C for stoichiometric mixtures give an Arrhenius plot, shown in Fig. 4. The apparent activation energy of the reaction is $E = 22.4$ kcal/mole, the pre-exponential factor being $A = 2.6 \times 10^9$/min.

For the surface of 22 m^2 of catalyst, the rate W of the reaction is then represented by the relationship:

$$W = 2.6 \times 10^9 \times [\exp(-22400/RT)] \, [H_2][C_2H_4]^0 \text{ molecules/min.}$$

The comparison with the homogeneous reaction according to the results of Pease (*7*):

$$W = 10^{-11} \times [\exp(-43150/RT)] \, [H_2][C_2H_4] \text{ molecules/sec} \quad (1)$$

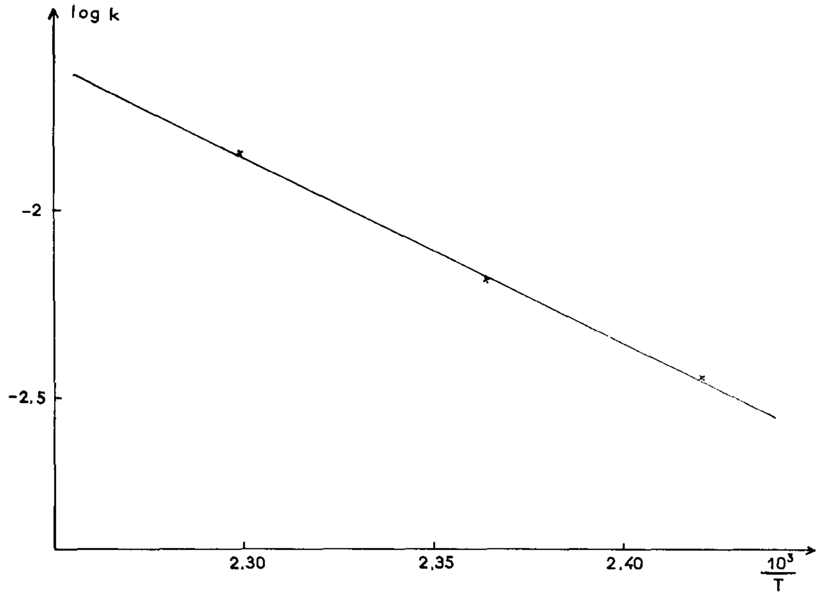

Fig. 4. Arrhenius plot for pure zinc oxide.

may be made after some transformations (*8*). For an equimolecular mixture of hydrogen and ethylene under 1 atm pressure:

$$[H_2] = [C_2H_4] = 2.5 \times 10^{19} \text{ molecules/cm}^3$$

The initial rate of the homogeneous reaction would be:

$$W_0 = 6 \times 10^{27} \times [\exp(-43150/RT)] \text{ molecules/cm}^3 \text{ sec} \quad (2)$$

In the same conditions of concentration, Eq. (1) concerning the catalytic reaction, becomes:

$$W_0 = 6.2 \times 10^{28} \times [\exp(-22400/RT)] \text{ molecules/cm}^3 \text{ min}$$

or

$$W_0 = 1 \times 10^{27} \times [\exp(-22400/RT)] \text{ molecules/cm}^3 \text{ sec}$$

The value of the initial rate of the heterogeneous reaction corresponds to 22 m^2 of catalyst. To compare it to the initial rate of the homogeneous reaction given by Eq. (2), it must be calculated for a surface of the mass of the catalyst contained in 1 cm^3. Introducing the specific surface, 31 m^2/g, and the specific weight, 5.6 g/cm^3, of zinc oxide, the initial rate of the heterogeneous reaction would be:

$$W_0 = 8 \times 10^{27} \times [\exp(-22400/RT)] \text{ molecules/cm}^3 \text{ sec} \quad (3)$$

Comparison of Eqs. (2) and (3) shows that zinc oxide decreases the activation energy from 43 to 22 kcal/mole, but the pre-exponential factor remains the same. The accelerating factor due to the catalyst is, at 423°K (150°C):

$$\exp[(43150 - 22400)/(R \times 423)] \simeq 10^6$$

Boudart (*8*) proposed a chain mechanism for the catalytic hydrogenation of ethylene by making an analogy with the homogeneous reaction for which a chain mechanism is well established (*9*). The calculation shown above gives further argument for this analogy. Taking into account the conclusions reached by kinetics studies the following chain mechanism between adsorbed species is proposed:

$$H_{2(ads)} \rightarrow 2H_{(ads)} \qquad \text{Initiation} \quad (4)$$

$$\left.\begin{array}{l} H_{(ads)} + C_2H_{4(ads)} = C_2H_{5(ads)} \qquad (5) \\ C_2H_{5(ads)} + H_{2(ads)} = C_2H_{6(g)} + H_{(ads)} \qquad (6) \end{array}\right\} \text{Propagation}$$

$$C_2H_{5(ads)} + H_{(ads)} = C_2H_{6(g)} \qquad \text{Interruption} \quad (7)$$

However the slow step (4) could be favored by the presence of adsorbed ethylene according to:

$$H_{2(ads)} + C_2H_{4(ads)} \rightarrow H_{(ads)} + C_2H_{5(ads)} \qquad \text{Initiation} \quad (4a)$$

This scheme suggests that the catalyst allows the substitution of the easier path (4) or (4a) for the highly energetic initiation step in the homogeneous reaction:

$$H_2 + C_2H_4 \rightarrow C_2H_5 + H$$

Poisoning by Oxygen and Activity of Doped Catalysts

If the zinc oxide, instead of being heated *in vacuo* at 250°C, is heated in 160 mm of oxygen at the same temperature, it does not show any catalytic activity in the hydrogenation of ethylene between 150° and 200°C. However the oxygen-treated catalyst recovers the initial activity after activation *in vacuo* at 250°C (Fig. 5). Actually, the activity is already very much decreased if at 150°C only 0.5 mm of oxygen is admitted for a few minutes.

The electric conductivity studies have shown (*2*) that vacuum treatment of zinc oxide at 250°C leads to the formation of a nonstoichiometric zinc oxide:

$$Zn^{2+}O^{2-} \rightleftarrows Zn_i + \tfrac{1}{2}O_{2(g)} \rightleftarrows Zn_i^+ + e^- + \tfrac{1}{2}O_{2(g)}$$

where Zn_i is a surface "interstitial" zinc.

The adsorption of hydrogen on an evacuated zinc oxide (which is catalyst) is essentially covalent (*2*) and can be visualized as occurring on Zn^+ sites (*10*):

$$Zn_i^+ + \tfrac{1}{2}H_2 \rightleftarrows (Zn - H)^+$$

The adsorption of hydrogen on a stoichiometric oxide (which is not catalyst) involves ionization (2) according to the equilibrium:

$$\tfrac{1}{2}H_2 + O^{2-} \rightleftarrows OH^- + e^-$$

It would therefore appear that only

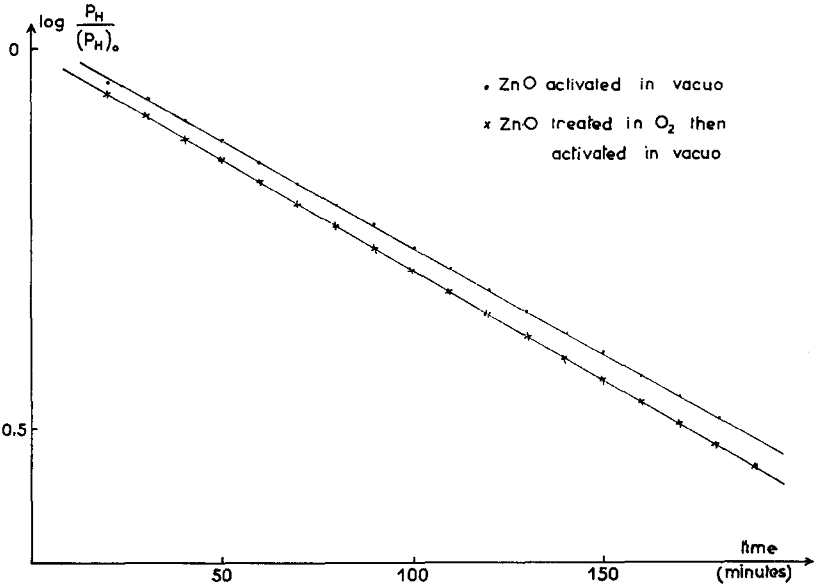

FIG. 5. Influence of activation of the catalyst *in vacuo* after poisoning by oxygen.

covalent hydrogen can participate in the reduction of ethylene. The purpose of the activation treatment *in vacuo* is then to produce, at least at the surface, the nonstoichiometric zinc oxide, a necessary condition for the catalytic activity.

The catalysts doped by lithium or by gallium must also be activated *in vacuo* at 250°C to exhibit a catalytic activity at 150°C. The kinetic results in the hydrogenation of ethylene given in Table 2, and for one temperature (162°C), shown in Fig. 6, give evidence that doping does not influence the catalytic activity of the zinc oxide. The

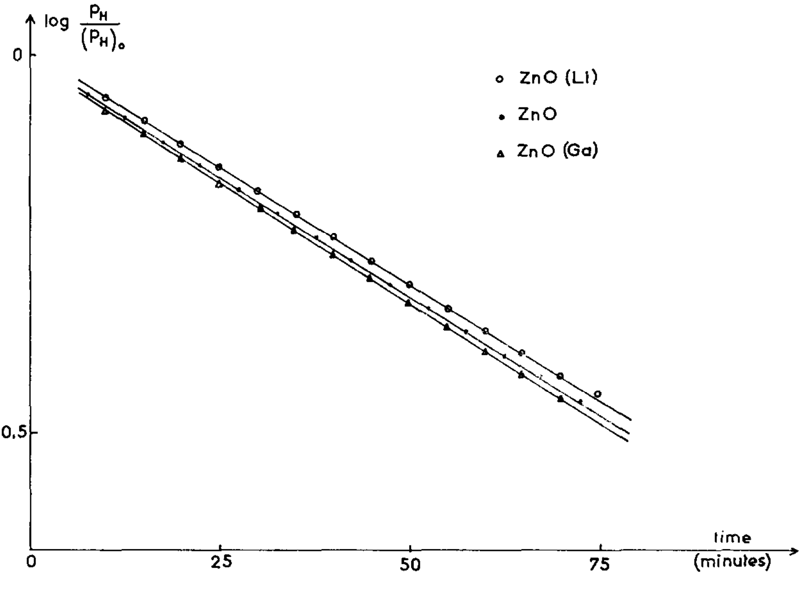

FIG. 6. Influence of doping on the rate constant.

TABLE 2
KINETIC CONSTANTS FOR PURE AND DOPED ZINC OXIDE

Catalyst	Rate constant (min^{-1}) 140° C	150° C	162° C	Activation energy (kcal/mole)
ZnO (Li)	3.5×10^{-3}	6.2×10^{-3}	1.4×10^{-2}	22
ZnO	3.6×10^{-3}	6.5×10^{-3}	1.4×10^{-2}	22
ZnO (Ga)	3.7×10^{-3}	6.5×10^{-3}	1.5×10^{-2}	22

rate constants and the activation energies are identical for the three cases.

In the same way as for pure oxide, doped oxides are poisoned by oxygen and fully regenerated by activation *in vacuo* at 250°C.

These results confirm the role previously attributed to the activation treatment of the catalyst *in vacuo*. The formation of a nonstoichiometric oxide is a necessary condition for the catalytic activity in the hydrogenation of ethylene. This formation is accompanied by an increase of the concentration of free (conductivity) electrons. Doping by lithium or by gallium, respectively, decreases or increases this concentration in the oxide and changes the activation energy of conductivity (*2*). However, the catalytic activity of the catalysts is independent of these modifications. It would then appear that the rate-determining step does not involve a charge transfer between the solid and the reagents. The electronic structure of the catalyst is therefore without influence on the catalytic activity.

It is then concluded that the activity in the hydrogenation of ethylene exhibited by the activated zinc oxide and its electric conductivity due to free electrons, are parallel but not correlated properties of a nonstoichiometric zinc oxide. To find a correlation emphasis should be given to the nature of chemisorbed species, hydrogen and ethylene. Only covalent complexes, formed without the electron transfer to the conductivity band (*2*), are reactive in catalysis at 150°C.

One is led to think that a relationship between electronic structure and catalytic activity would be observed at temperatures when hydrogen is preferentially adsorbed in ionic form. For reactions with oxygen, which is always adsorbed in ionic form, this relationship would be observed more easily. However it seems wise to expect that the type of correlation for a given catalyst may vary with the temperature of the reaction and also with the type of the reaction.

ACKNOWLEDGMENT

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