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Effects of Metallic Surfaces on the Thermal Decomposition of Ethane

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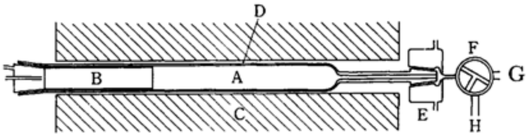
The thermal decomposition of ethane was conducted in a static system at 700°C, using a silica vessel packed with a sheet of metal. Various sorts of metals were tested. The rate of ethylene formation decreased notably in the presence of metals as compared with the rate in an unpacked vessel, the decrease being larger at lower pressures. The activity of metals to reduce the rate was in order: Zr$>$Ti$>$Fe$>$Cu$>$W,Ag$>$Pt,Mo. The rate of methane formation did not change with the packing of metals. The main reactions were assumed to be radical reactions in the gas phase. From the observed order of reaction, it was concluded that the action of metal is to catalyze the recombination of hydrogen atoms and therefore to terminate the radical-chain reactions. A similar action was noted in hydrogen dissolved in a titanium sheet.

A metallic surface placed in hydrocarbon gases at a high temperature may catalyze the decomposition of the hydrocarbon on the surface. There is also another aspect of influence, which is the subject of the present report, *i. e.*, the metal surface may alter the rate of radical reactions in the gas phase by taking part in the formation and the quenching of radicals. This type of catalytic behavior of the reactor wall was first suggested by Rice and Herzfeld.[1] Laidler and Wojciechowski[2] attributed the change in the reaction order of ethane decomposition by the increase of the surface-to-volume ratio of quartz reactors to the termination process at the wall. Marshall and Quinn[3] made a kinetic analysis of ethane decomposition, assuming that homogeneous quadratic and heterogeneous linear termination occur simultaneously. The dependence of the rate of propane decomposition on the nature and the area of the surface was shown by Voevodsky.[4] However, no metallic surface seems to have been examined, so the present investigation was undertaken in order to clarify whether metals accelerate or retard the decomposition and to correlate the observed effects with the nature of the surface.

Experimental

Apparatus. The decomposition was carried out by a static method using a silica reaction vessel (shown in Fig. 1), which had a volume of 8.6 cc and an effective surface area of 31.6 cm². To see the effect of the metal, sheets of various metals, rectangular in shape and 0.1 mm thick, were bent and packed in turn into the vessel. Three different sizes of sheets were used: S-1, 1.0×7.0 cm²; S-2, 2.0×7.0 cm², and S-3, 4.0×7.0 cm². The packed states of the sheets are illustrated in Fig. 1. The packing of a silica plate was used for comparison. The reaction vessel was placed in an electric furnace and was maintained at 700±2°C for whole runs.



(a) Arrangement

(b) Cross sections of packed reactor

Fig. 1. Reaction vessel.

A: space for reaction, B: silica plug to exclude the space in temperature gradient, C: electric furnace, D: thermocouple, E: water-cooled joint, F: switching valve, G: piping connected to reservoir, H: piping connected to expansion bulb.

Materials. A research-grade ethane (>99.7%) was frozen in liquid air, and the non-condensable gases were removed by evacuation; then the ethane was evaporated slowly to leave the heavier impurities and was led into a reservoir. The metals used were obtained from commercial sources and were at least 99.9% pure, with the exception of titanium (99.3%). The pretreatment of metals will be individually described below.

Procedure. After the evacuation of the reaction vessel, ethane was introduced into the vessel and the pressure was equilibrated with that of the reservoir. This pressure will be referred to as the initial pressure of ethane, p_0. The reaction was stopped by expanding the gas in the reaction vessel into a pre-evacuated bulb

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[1] F. O. Rice and K. F. Herzfeld, *J. Phys. Colloid Chem.*, **55**, 975 (1951).

[2] K. J. Laidler and B. W. Wojciechowski, *Proc. Roy. Soc.* (*London*), *Ser. A*, **260**, 91 (1961).

[3] R. M. Marshall and C. P. Quinn, *Trans. Faraday Soc.*, **61**, 2671 (1965).

[4] V. V. Voevodsky, *ibid.*, **61**, 2671 (1965).

(320 cc), and then the product was compressed by the use of a Teopler pump into the sampling tube of the gas chromatograph and analyzed.

Four to eight runs were made at the same pressure of ethane. The reaction time was usually 2 to 10 sec, and less than 20% of the ethane was decomposed. The gas chromatograph was equipped with 1.5 m of an active alumina column at 30°C; helium was used as the carrier, and the amounts of hydrogen, methane, ethane, and ethylene were determined quantitatively.

Results

Main Course of Reaction. The gaseous products were composed of nearly equal moles of ethylene and hydrogen, a small amount of methane (4 to 10% of ethylene), and unreacted ethane. In the cases of titanium or zirconium packing, the yield of hydrogen was somewhat less than that of ethylene, perhaps because of the dissolution of hydrogen into the metal. Also, the weight of these metals increased slightly, indicating that about 4% of the reacted ethane was fixed in a form of carbide. As the rate of the carbide formation of these metals with ethane is no less than that with ethylene,[5] the surface decomposition may be supposed not to disturb the gaseous-product distribution. In the other metals, no measurable change in the weight was observed and a lustrous appearance was retained. From these facts and from a tendency of the results described below which seems reasonable, it was assumed that the course of the decomposition in the gas phase in the presence of metal surface was similar to that reported for the reaction in silica vessels, at least so far as the initial rates were concerned.

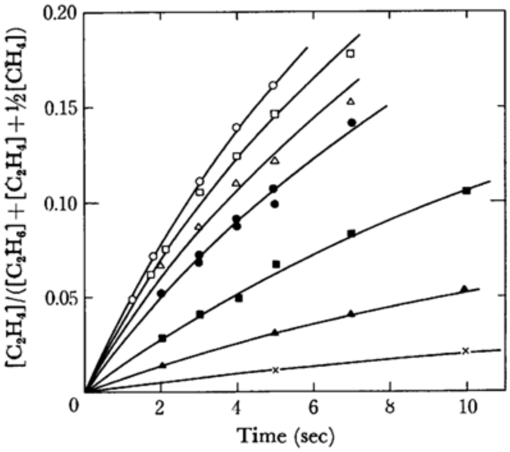

Fig. 2. Ethylene yield against time, in the presence of iron (S-2).
The p_0 values are: ○ 425, □ 288, △ 213, ● 153, ■ 73, ▲ 39, × 19 mmHg

The ethylene yield-time curve for each p_0 was similar to the reported pattern.[2] Typical plots are shown in Fig. 2. From the initial slope of the plots in Fig. 2, the initial rate of ethylene formation, r_0, was determined.[6] The initial rate of methane formation, r_0', was obtained in a similar manner. The rates so obtained have a probable error of about 10%, which is allowable for the present purposes.

Rate of Ethylene Formation. The rate of ethylene formation in the silica vessel is plotted against p_0 in the logarithmic scale in Fig. 3. This shows that the reaction is nearly first order with respect to ethane at higher pressures and 3/2 at

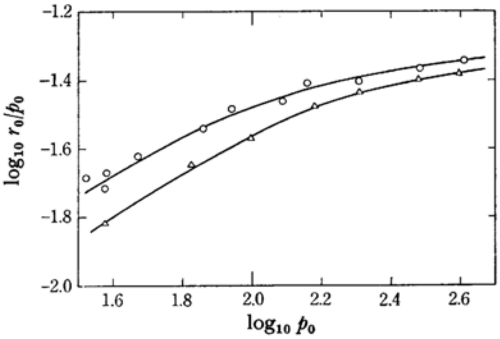

Fig. 3. Rate of ethylene formation in silica vessel.
○ unpacked (S/V=3.7 cm^{-1})
△ packed with a plate (S/V=7.1 cm^{-1})

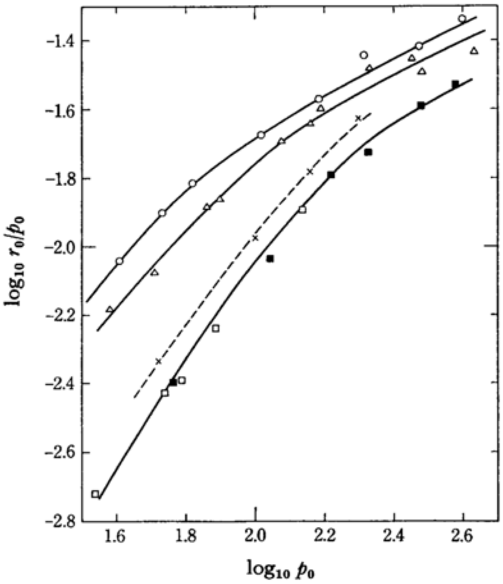

Fig. 4. Rate of ethylene formation in the presence of iron.
○ S-1, △ S-2 normal, × S-2 abraded, □ S-3 normal, ■ S-3 without hydrogen reduction

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[5] Y. Tamai, Y. Nishiyama, A. Abe and M. Takahashi, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **72**, 1933 (1969).

[6] The initial slope itself means r_0/p_0 and this is used in preference to r_0 for convenience.

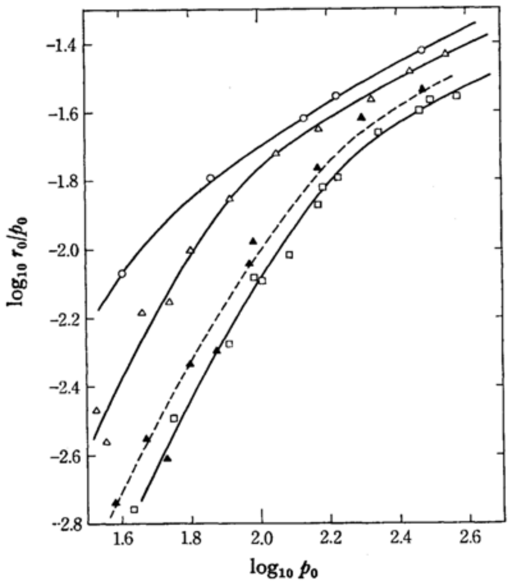

Fig. 5. Rate of ethylene formation in the presence of titanium.
○ S-1, △ S-2, ▲ S-2 with dissolved hydrogen, □ S-3

lower pressures, and that the order is altered slightly by the increase in the surface area, though the reaction rate is reduced somewhat.

The results for the cases of packing with iron sheets are shown in Fig. 4. Before use, the packed sheets were normally heated in 200 mmHg of hydrogen at 700°C for 30 min in order to reduce the oxidized surfaces. The same treatment was repeated frequently between the decomposition runs to keep the surface clean. A few runs were carried out using an iron sheet which had not been treated with hydrogen, but they showed essentially the same trend. The rate was decreased markedly by the packing of iron, and the order of reaction was 2 to 5/2 at 50 mmHg, the larger order for the larger sheet.

A check was made on the surface roughness by using an iron sheet abraded by Emery paper (#1). The results show a more pronounced decrease in the rate.

The titanium sheets were normally used without hydrogen treatment, for this is irrelevant to the reduction of oxide. The effect of hydrogen was tested by using titanium sheets packed in the reaction vessel and equilibrated with about 300 mmHg of hydrogen at 700°C (110 cc STP/g was absorbed). After this, the vessel was evacuated for 5 min and ethane decomposition conducted as usual.

The packing of titanium exerted an influence on the rate similar to that of iron, as is shown in Fig. 5, but the effect was more remarkable. The reaction order at 50 mmHg was from 2.1 to 3.0. It is interesting to note that titanium with dissolved hydrogen behaved as if the area of the sheet had been enlarged.

Various metals with the same dimensions are compared in Fig. 6. All the metals had smooth surfaces, and copper, silver, and platinum were treated with hydrogen, as iron had been. In every case, the rate was more or less reduced and the activity was in the order: $\mathrm{Zr} > \mathrm{Ti} > \mathrm{Fe} > \mathrm{Cu} > \mathrm{W} \cong \mathrm{Ag} > \mathrm{Pt} \cong \mathrm{Mo}$.

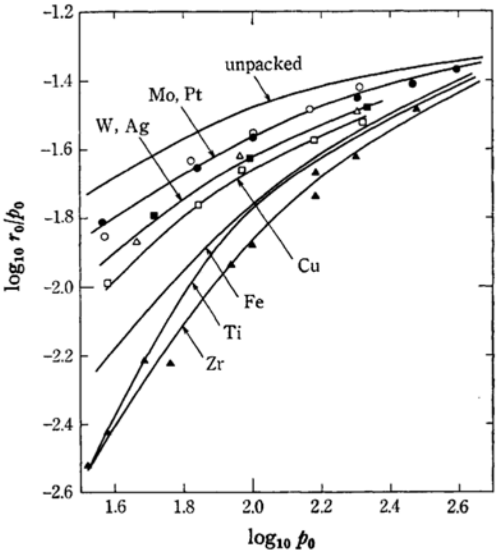

Fig. 6. Comparison of metals.
▲ Zr, □ Cu, △ W, ■ Ag, ○ Mo, ● Pt;
S-2 for each

Rate of Methane Formation. The rates of methane formation in several cases are shown in Fig. 7. This figure indicates that the rates are only slightly affected by the presences of metallic surfaces, in contrast to the simultaneous large variation in the rate of ethylene formation. The reaction order was approximately 3/2 at higher pressures and increased to about 2 as the pressure was reduced.

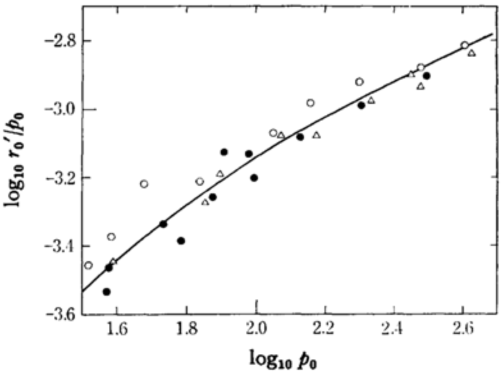

Fig. 7. Rate of methane formation.
○ unpacked, △ packed with iron S-2, ● Packed with titanium S-2 with dissolved hydrogen

Discussion

Kinetic Consideration of the Reaction Order. The thermal decomposition of ethane in the gas phase is usually explained on the basis of the radical mechanism as follows:

$$C_2H_6 \rightarrow 2CH_3\cdot \quad (1)$$

$$CH_3\cdot + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot \quad (2)$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot \quad (3)$$

$$H\cdot + C_2H_6 \rightarrow H_2 + C_2H_5\cdot \quad (4)$$

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_4H_{10} \text{ or } C_2H_6 + C_2H_4. \quad (5)$$

The rate of methane formation is said to be a measure of the initiation step.[7] The order of this reaction was from 3/2 to 2 under the present condition; this order is in accord with the pressure-dependent nature of reaction (1).[7-9] The secondary production of methane from ethylene was noted in some cases,[10-12] but this is less important at present, for the rate of methane formation differed little among the cases in which the rate of ethylene formation differed remarkably.

The order of the decomposition of the ethyl radical is said to change from 1 to 3/2 as the pressure is reduced.[8,13] For the termination, the following processes involving hydrogen atoms were taken into account in addition to (5):

$$H\cdot + C_2H_5\cdot \rightarrow C_2H_6 \quad (6)$$

$$H\cdot + H\cdot \rightarrow H_2 \quad \text{(2nd order)} \quad (7)$$

$$H\cdot \rightarrow H_{ad} \text{ or } {}^1/_2\, H_2. \quad \text{(1st order)} \quad (8)$$

The reaction (6) is said to be quite slow in the gas phase.[8,14] The step (7) corresponds to a situation in which concentration of adsorbed hydrogen on the metal surface is relatively small and is in equilibrium with that in the gas phase. The step (8) reflects the situation either when the surface coverage of the adsorbed hydrogen is near unity and the recombination of hydrogen atoms occurs in the Rideal mechanism, or when every hydrogen atom is trapped by the surface when it collides.

For each case, the order of ethylene formation with respect to ethane was calculated, assuming the predominance of a particular termination step; the results are tabulated in Table 1.

TABLE 1. CALCULATED REACTION ORDER

Order of (1)	Order of (3)	Overall order for termination by (5)	(6)	(7)	(8)
3/2	1	3/4	5/4	7/4	5/2
3/2	3/2	5/4	3/2	7/4	5/2
2	1	1	3/2	2	3
2	3/2	3/2	7/4	2	3

The involvement of hydrogen in the termination increases the reaction order, as has been supposed by Marshall and Quinn[3] and others.[8,13] The present results seem to show clearly the contribution of hydrogen in termination. The highest order observed was 3 for titanium packing at lower pressures; it can be explained by the linear termination of hydrogen atoms. At higher pressures, termination by (6) seems to predominate. The order in the presence of iron indicates that the recombination of hydrogen is between linear and quadratic concentration dependence.

Other Possible Contributions of Metals. There is a possibility that the metallic wall initiates the radical chain. However, methyl radical formation seems not to occur on metal surfaces, as the rate of methane formation is scarcely affected by metals. Another mode of initiation might be the inverse step of (6), but this could play a role only at a very early stage of the decomposition, since the radical concentrations at the steady state favor recombination.

Also, the heterogeneous dehydrogenation of ethane might take place to some extent. However, at present this cannot be discriminated from homogeneous processes, as metallic surfaces exerted a stronger influence on termination, resulting in a reduction of the overall rate over the entire pressure range.

Effects of the Nature of the Surfaces. If the above explanation is correct, the negative catalytic activity of metals might have a close correlation with that of the recombination of hydrogen atoms in a hydrogen atmosphere. However, this activity would depend on the state of the surface. For a quantitative comparison, it is necessary to define the geometry of packing and to ascertain the rate of diffusion of each component. The metal surfaces in the present experiment were by no means clean and the crystallographic characteristics were not defined, so only a qualitative discussion is possible here. In spite of these imperfections, the present trend among metals seems reasonable and is, though only partly, in accord with that reported by Wood and Wise;[15] *i. e.*, the catalytic activity of metals for hydrogen-atom recombination is roughly in the order: Ti>(Ni)>

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[7] A. B. Trenwith, *Trans. Faraday Soc.*, **63**, 2452 (1967).

[8] A. B. Trenwith, *ibid.*, **62**, 1538 (1966).

[9] M. C. Lin and M. H. Back, *Can. J. Chem.*, **44**, 2537 (1966).

[10] C. P. Quinn, *Proc. Roy. Soc.* (*London*), *Ser. A*, **275**, 190 (1963).

[11] C. P. Quinn, *Trans. Faraday Soc.*, **59**, 2543 (1963).

[12] M. C. Lin and M. H. Back, *Can. J. Chem.*, **44**, 2369 (1966).

[13] M. C. Lin and M. H. Back, *ibid.*, **44**, 505 (1966).

[14] D. W. Setser and B. W. Rabinovitch, *J. Chem. Phys.*, **40**, 2427 (1964).

[15] B. J. Wood and H. Wise, *J. Phys. Chem.*, **65**, 1976 (1961).

Cu>W>Pt. The packing of a nickel sheet was attempted in this study, but the reaction rate varied considerably from run to run, so it was impossible to determine the rate with the desired precision. Roughly speaking, however, the effect of nickel was in the same range as that of iron. The accordance except in the case of nickel seems to indicate that the catalytic action of metals for hydrogen recombination is relatively insensitive to the adsorbed hydrocarbons. The weak activity of molybdenum may be associated with the weak interaction of this with hydrogen.16)

The above trend holds only for metals of similar appearance; alteration of the surface state by abrasion changed the activity, as is usual in catalysis.

The action of hydrogen dissolved in titanium can be interpreted by assuming that hydrogen atoms emerging from bulk metal combine much more easily with hydrogen from the gas phase. The enhanced activities of dissolved hydrogen were noted in the the recombination of hydrogen atoms15) and in other reactions, for example, in the dehydrogenation of cyclohexane.17)

The author is grateful to Professor Yasukatsu Tamai for his helpful discussions and encouragement.

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16) The solubility of hydrogen in molybdenum is less than that in silver, at 700°C; S. Dushman and J. M. Lafferty, "Scientic Foundation of Vacuum Technique," 2nd ed., John Wiley and Sons, New York (1962), p. 537.

17) B. J. Wood, *J. Catalysis*, **11**, 30 (1968).