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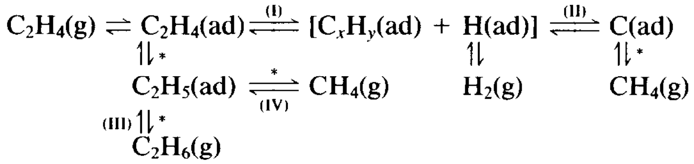
Role of Hydrogen in Catalytic Decomposition of Ethylene on Nickel

Carbon deposition on transition metals by the decomposition of hydrocarbons has been the subject of many studies. In the course of these experiments, the enhancement of the deposition rate by the presence of H_2 in the decomposition atmosphere has been found in the case of Ni catalysts (*1*–*3*). Possible explanations for this effect were presented by Lobo *et al.* (*4*) and Nishiyama and Tamai (*5*). In order to clarify this problem, we have made an attempt to remove H_2 selectively from the reacting system using a Ti trap.

The decomposition of C_2H_4 was carried out in a conventional closed-circulation system fitted with a quartz spring balance to obtain the weight change due to the carbon deposition on Ni catalyst. The apparatus is shown in Fig. 1. It is known that Ti rapidly absorbs much hydrogen above 400°C (*6*). The trap (Ti sponge, 99.5% purity, Nakarai Chemicals Ltd.) was suitably arranged in the flow path of the system. Before the experiments, 1 g of Ti in the trap was heated in H_2 (50 Torr) at 550°C for 1 hr and then outgassed. The trapping of H_2 during the reaction was usually done at 450°C. The reactions were carried out at an initial pressure of 100 Torr in the range of 400–500°C. Constituents in the gas phase were analyzed by a gas chromatograph (silica gel column and He as carrier gas) at fixed intervals of time during the reaction. The catalyst was in the form of ribbon. The preparation and pretreatment of the catalyst, and the purification of gases used in the present experiment were described previously (*7*). It was confirmed by gravimetry that under the present conditions the Ti sponge adsorbs no hydrocarbons and no carbon deposition occurs on the sponge.

Figure 2 shows a typical time course of the reaction obtained without the trapping of H_2 at 450°C. The reaction goes essentially the completion and the products detected during the reaction are H_2, C_2H_6, CH_4, and carbon which remains on the surface of the catalyst. It is seen qualitatively that after a short induction period the amounts of H_2 and carbon increase, pass through a maximum, and gradually decrease in the later stage. These decreases are attributed to the hydrogenation of the deposited carbon. The amount of C_2H_6 passes through a maximum, ending at zero. The rate of formation of CH_4 is approximately proportional to the amount of C_2H_6: it is zero initially, passes through a maximum when the amount of C_2H_6 is at maximum, and gradually falls. The reaction is not effected with the extent of carbon deposition in agreement with other observations (*2*, *4*, *8*). Detailed consideration of this fact was made in their papers. A scheme including dehydrogenation, hydrogenation, and hydrogenolysis is given below which is found to be useful in explaining the present results. Here the symbols (ad) and (g) refer to adsorbed and gaseous species, and asterisks (*) denote the reaction with hydrogen.



$$\begin{tikzcd}
C_2H_4(g) \arrow[r, phantom, "\rightleftharpoons"] & C_2H_4(ad) \arrow[r, phantom, "\overset{\mathrm{(I)}}{\rightleftharpoons}"] \arrow[d, shift left, "*"] \arrow[d, shift right, leftarrow] & {[C_xH_y(ad)} & {+\ H(ad)]} \arrow[r, phantom, "\overset{\mathrm{(II)}}{\rightleftharpoons}"] \arrow[d, shift left] \arrow[d, shift right, leftarrow] & C(ad) \arrow[d, shift left, "*"] \arrow[d, shift right, leftarrow] \\
 & C_2H_5(ad) \arrow[r, shift left, "*"] \arrow[r, shift right, leftarrow, "\mathrm{(IV)}"'] \arrow[d, shift left, "*"] \arrow[d, shift right, leftarrow, "\mathrm{(III)}"'] & CH_4(g) & H_2(g) & CH_4(g) \\
 & C_2H_6(g) & & &
\end{tikzcd}$$

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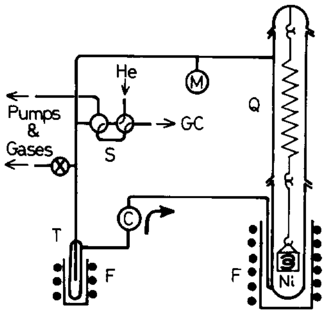

FIG. 1. Experimental system. C, Circulating pump; F, furnace; M, manometer; Q, quartz spring balance; S, sampling loop; T, Ti trap.

Figure 3 shows a result obtained by use of Ti trap. It is seen that despite 50% or above of the reactant, C_2H_4, remaining in the reaction system after about 500 min, the rate of carbon deposition falls to near zero in the absence of H_2 (The residual partial pressure was of the order of 10^{-1} Torr.) Although small amount of C_2H_6 was produced at first, no CH_4 was detected in the gas phase. The reaction features were affected, of course, by the position of the trap in the flow path and by the rate of absorption of H_2. In fact, when the trap was placed near the catalyst and 5 g of the sponge was used in order to remove thoroughly the H_2 during the experiment, the reaction stopped at 5% conversion and no gaseous products were detected. These findings indicate that the gaseous H_2 contributes to the formation of C_2H_6 and CH_4 through mainly Steps III and IV. It is likely that adsorbed hydrogen atoms desorb rapidly when the gaseous H_2 is removed from the reacting system. The dehydrogenation of olefin (Step I), on a Ni surface seems to take place easily in the absence of gaseous H_2 (*9*). It is concluded that the process of hydrogenolysis (Step II), is important for the overall reaction. This explanation is consistent with the suggestions proposed by Lobo *et al.* (*4*) and Nishiyama and Tamai (*5*). We believe that the method used in the present study is effective for the elucidation of the mechanism of catalytic reactions involving H_2 as a reaction product.

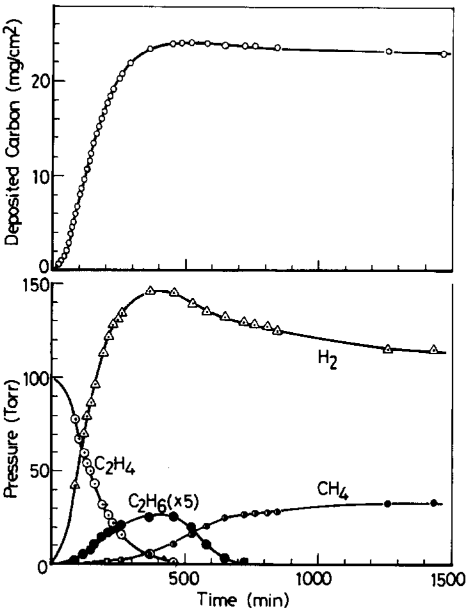

FIG. 2. Changes in partial pressures of reactant and products, and carbon deposition during reaction obtained without trapping of H_2 (reaction temperature, 450°C).

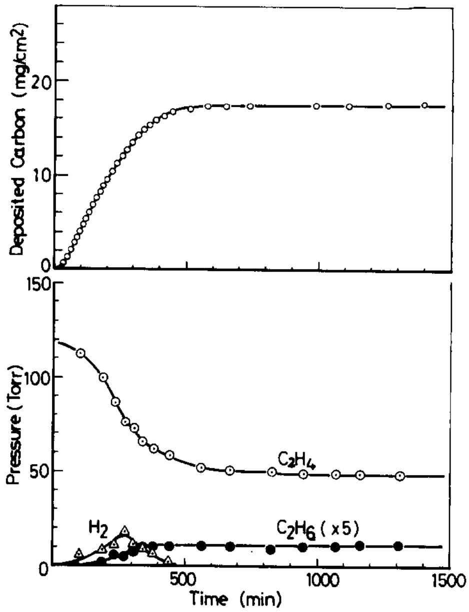

FIG. 3. Changes in partial pressures of reactant and products, and carbon deposition during trapping of H_2 (reaction temperature, 450°C).

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