Nature of Active Site on Cobalt Oxide as Revealed by Tracered and Competitive Reactions of Ethylene and Butene and by H_2–D_2 Equilibration

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Prechemisorption of hydrogen on cobalt oxide gives rise to an extraordinarily active hydrogen for both isotopic exchange of ethylene and isomerization of butene, while the active part of prechemisorbed hydrogen is consumed within a short period to form butane as demonstrated by incorporation of prechemisorbed deuterium into butane. Both the ethylene and butene reactions take place on the common site of the active hydrogen as evidenced by an intermolecular hydrogen transfer in competitive runs. The competitive reaction discloses that ethylene is more strongly adsorbed than butene, and hence that the reacting olefin molecule is directly coordinated to cobalt ion prior to the reaction with hydride to form the alkyl-intermediate. The previously observed enhancements by hydrogen of butene isomerization and isotopic exchange of ethylene are ascribed to the formation of active hydrogen. No similar effect was found for H_2–D_2 equilibration at −195 and −78°C and for ethylene hydrogenation at room temperature.

INTRODUCTION

In a previous paper from this laboratory it was shown that the adsorbed intermediate of olefin hydrogenation over the dehydrated surface of cobalt oxide is a π-complex formed on exposed cobalt ion (*1*). It was also shown that both the isotopic exchange of C_2H_4 and C_2D_4 and the isomerization of butene are accelerated by the presence of gas phase hydrogen, demonstrating the participation of alkyl intermediate formed by reaction with the chemisorbed hydrogen (*2*). Moreover, a part of prechemisorbed hydrogen was found to enhance the isomerization strikingly, whereas the rapid reaction terminates within a short period.

The nature of this prechemisorbed active hydrogen is of interest in connection with

Siegel's model of active site on oxide surface (*3*), which was proposed on the basis of catalysis on the cobalt oxide. It is expected that the investigation of this active hydrogen is helpful to elucidate the nature of active sites over cobalt oxide.

EXPERIMENTAL

The procedures of preparation of oxide sample and of pretreatment with hydrogen were the same as before (*2*) and unless otherwise stated the amount of catalyst used was 15 g (total area 38.6 m²). The oxide samples before and after the hydrogen treatment are called "fresh" and "stabilized" catalysts, respectively. The apparatus employed was a closed circulating system of about 225 ml. Unless otherwise stated, the pretreatment was made with

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70 mm Hg of hydrogen at 25°C, and the reaction temperature, too, was usually 25 °C.

Deuterium, ethylene, and cis-butene of more than 99% purity were purchased from Takachiho Shoji Co. and deuteroethylene from Merck Sharp & Dohme Canada Ltd. Olefins were freed from permanent gases by solidification at liquid nitrogen temperature followed by evacuation. Analyses were made by gas chromatography and mass spectrometry.

The initial rates of both butene isomerization and C_2H_4–C_2D_4 exchange reaction were estimated from the equation

$$R = -2.3(N/Wt) \log (1 - X),$$

where W, N, and t denote the amounts of catalyst and reactant and reaction time, respectively, and X denotes the fractional attainment of equilibrium for the isomerization or the isotopic exchange defined by

$$X = (x_0 - x_t)/(x_0 - x_e),$$

where x_0, x_t, and x_e denote the mole fractions of C_2D_4 or cis-butene at times zero, t, and equilibrium.
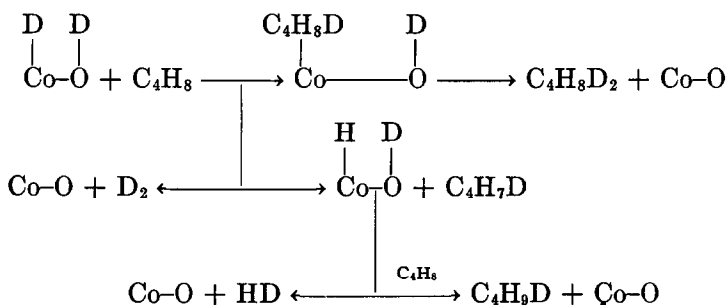
RESULTS

1. Preparation and Consumption of the Active Hydrogen

As reported in the previous papers, the fresh catalyst dehydrated at 400°C reacts with hydrogen at room temperature at first rapidly and later slowly (4) and a part of the irreversibly adsorbed hydrogen shows a high activity for the isomerization of butene (2). This active part of adsorbed hydrogen is called here the active hydrogen. When the fresh catalyst was treated with hydrogen for 16 hr followed by evacuation for 5 hr, the initial rate of cis-butene isomerization was estimated using the above equation to be 0.63 ml stp/min g, whereas the rapid isomerization terminated within 2 min and changed to a much slower one. The second run made after evacuation of butene at 25°C gave the slower rate from the beginning, whereas the rapid rate was reproduced by the hydrogen treatment made on the deactivated sample. Thus it is likely that the active hydrogen is consumed during the butene isomerization.

The fate of active hydrogen was examined by using a larger amount of catalyst (30 g), which was treated with D_2 for 16 hr followed by evacuation for 5 hr. Cis-butene (1.7×10^{-1} mmol) was circulated on this D_2 prechemisorbed catalyst for 3 min. The products were separated by gas chromatography. A small amount of butane (1.3×10^{-3} mmol) was found in addition to hydrogen with an approximate ratio of butane/hydrogen = 6. The amount of butane divided by the surface area is 1×10^{12} molecule/cm², which is of the same magnitude as the number of active sites (1.3×10^{12}) as estimated by CO poisoning of ethylene hydrogenation (4). Mass spectrometric analysis of butane showed a one-to-one mixture of d_1 and d_2. The hydrogen gas formed was also found to be highly deuterated ($HD/D_2 = \frac{1}{3}$). These results are consistent with the following scheme, previously proposed (2).

$$
\begin{array}{c}
\overset{D}{\underset{|}{}}\ \overset{D}{\underset{|}{}} \\
Co\text{–}O + C_4H_8 \longrightarrow Co\text{——}O \longrightarrow C_4H_8D_2 + Co\text{–}O
\end{array}
$$

It is accordingly concluded that the
active hydrogen is mainly consumed by the
formation of butane-giving deactivated sur-
face that is reactivated by hydrogen treat-
ment or by the presence of hydrogen in gas
phase as demonstrated by the hydrogen
enhancement of isomerization (2). If the
lifetime of active hydrogen during the
butene isomerization is determined by the
rate of butane formation as expected from
the above conclusion, it should be longer
at lower temperatures. Indeed, a lifetime of
more than 10 min was observed at −25°C.

Since the active hydrogen can be restored
by the hydrogen treatment of deactivated
catalyst, it seemed possible to determine
the amount of active hydrogen by adsorp-
tion measurements. The amount of adsorp-
tion during the second hydrogen treatment
was very small, around 0.1 μmol/g. Further-
more, an initial fast adsorption, the amount
of which was dependent on the evacuation
condition, was followed by a slow adsorp-
tion of $1 \sim 5 \times 10^{11}$ molecules/hr cm^2 at
25°C. The latter seemed to produce the
active hydrogen.

Thus the effect of hydrogen treatment
time and temperature on the initial rate of
isomerization was examined. Namely, the
deactivated catalyst was submitted to
treatment with hydrogen (70 mm Hg) at
temperatures 0, 25, and 50°C and for
different times (0.5, 1, and 2.5 hr), followed
by 1 hr of evacuation at 25°C. The isomeri-
zation activity of thus-prepared catalyst
was tested with cis-butene at 25°C. Be-
tween runs the butene over the catalyst
was evacauted at 25°C for 0.5 hr, which
was confirmed to be enough to remove
butene.

The time courses of trans-butene for-
mation are shown in Fig. 1, where the
catalyst was treated under different con-
ditions. It is obvious that the very rapid
isomerization terminates within about 1.5
min independent of the treatment condition
and is followed by a slow isomerization.
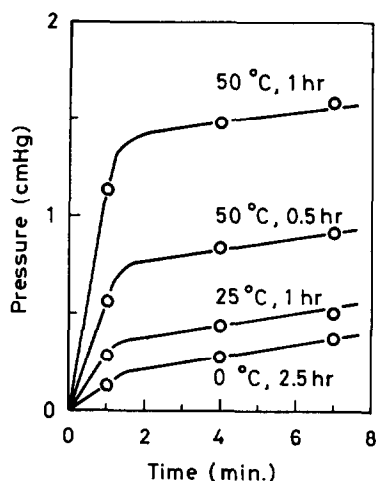Although the rate of slow isomerization is

FIG. 1. Time course of trans-butene formation
over Co$_3$O$_4$ pretreated with H$_2$ under different
conditions.

also independent of the treatment condi-
tion, the rate of rapid isomerization in-
creases with the time and temperature of
pretreatment, indicating that the initial
rate of isomerization reflects the amount of
hydrogen chemisorbed in the pretreatment.
Since the duration of the initial rapid pro-
cess is unaffected by the treatment con-
dition and thus by the amount of active
hydrogen, those hydrogen atoms are likely
to be independent of each other, being
individually consumed within a definite
time by the reaction with butene.

If the initial rate of isomerization is
proportional to the amount of active hy-
drogen, relative values of the rate of
chemisorption to form the active hydrogen
may be estimated from the variation of
initial rate of isomerization with the pre-
treatment conditions. The initial rates of
cis-butene isomerization (R) are obtained
from runs in Fig. 1 and are divided by the
pretreatment time t to give R/t. Both
values are shown in Table 1 as a function
of pretreatment condition. The ratio R/t
increases with an increase in pretreatment
temperature and the Arrhenius plot of R/t
is approximately linear, as shown in Fig. 2;

TABLE 1

THE INITIAL RATE (R) OF *cis*-BUTENE ISOMERI-
ZATION AT 25°C ON COBALT OXIDE TREATED
AT TEMPERATURES FOR TIME t

Run	Temp. (°C)	Time (t) (hr)	Rate (R) (ml stp/ min g)	R/t
1	0	2.5	0.039	0.016
2	25	1.0	0.11	0.11
3	50	0.5	0.22	0.44
4	50	1.0	0.49	0.49

the apparent activation energy is 12 kcal/mol.

These results demonstrate that an activated adsorption of hydrogen takes place during the hydrogen treatment, giving rise to the active hydrogen, the amount of which controls the initial rate of isomerization. Thus it is clear that the amount of active hydrogen can be controlled at a fixed value by fixing the pretreatment condition.

2. Competitive Reaction of C_2H_4–C_2D_4 Exchange and Cis-Butene Isomerization

The active hydrogen as characterized above seems to be formed on cobalt ion to give a Co–H linkage. The insertion of butene to the Co–H bond would form butyl intermediate for the isomerization. The results in our previous paper (*2*) are consistent with this scheme. On the basis of coordination chemistry, Siegel assumed that the reacting olefin is coordinated to the cobalt ion prior to the insertion (*3*). If this is the case, it is expected that ethylene is more strongly coordinated than butene (*1*). There is, however, an alternative, where the olefin is adsorbed on oxide ion prior to the insertion. If this is the case, the relative strength of adsorption should be reversed (*1*). In order to examine the adsorption strength sequence of olefins, the competitive reaction of butene isomerization with the analogous reaction of ethylene, the C_2H_4–C_2D_4 exchange, was carried out with

the active hydrogen, taking advantage of nonoccurrence of hydrogenation.

The initial rate of isomerization decreased with increases in the evacuation time after the hydrogen treatment. For example, 1 and 15 hr evacuations resulted in 10 and 50% reductions, respectively, as compared with the rate obtained after 0.5 hr evacuation. Then the evacuation time was fixed to 0.5 hr in the subsequent runs.

After the deactivated catalyst produced by a run was treated with hydrogen for 2 or 15 hr at room temperature, an olefin mixture, $C_2H_4 : C_2D_4 : cis$-butene = 1:1:1.9 (toral pressure 52 mm Hg), was introduced over the catalyst. Conversions of olefins within the initial 1 min and the isotope distribution in the products are given in Table 2, together with percentage atomic D fractions, f_D, for the products, where percentage conversion denotes $100X$. It is disclosed that deuterium is transferred from ethylene to butene, as demonstrated by the increase in f_D for butenes (f_{D1}, f_{Dt}, f_{Dc}) accompanied by decrease in f_D for ethylene (f_{D2}). Although the deuterium distribution in ethylene for Run 2 largely deviates from symmetry with respect to d_4, this is consistent with the hydrogen transfer because C_2H_4–C_4H_8 transfer does not decrease d_0 while C_2D_4–C_4H_8 transfer decreases d_4. It is reasonable that the transfer is more
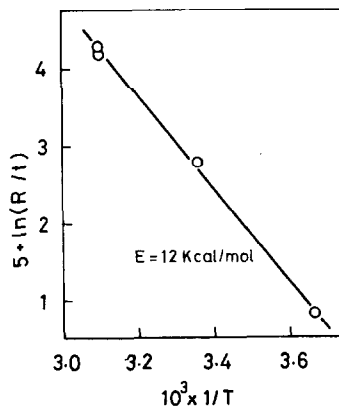

FIG. 2. Arrhenius plot of R_0/t.

TABLE 2

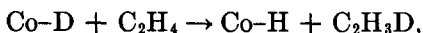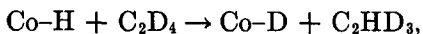COMPETITIVE REACTION OF C_2H_4–C_2D_4 EXCHANGE AND cis-BUTENE ISOMERIZATION OVER Co–H SITE[a]

Run	Duration of H_2 pre-treatment (hr)	Conversion (%)		Butene composition (%)			Atomic fraction (%)			
							Ethylene	Butene		
		Ex.	Iso.	1-C_4'	t-C_4'	c-C_4'	f_{D2}	f_{D1}	f_{Dt}	f_{Dc}
1	2	19.6	6.3	0.3	4.8	95.0	49.9	3.5	2.0	0
2	15	70.0	45.6	1.7	34.9	63.5	43.2	7.1	3.6	0.6

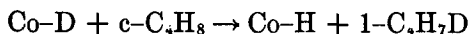| Run	Deuterium distribution (%)							
	Ethylene					d_1/butenes		
	d_0	d_1	d_2	d_3	d_4	1-C_4'	t-C_4'	c-C_4'
1	42	8	1	8	42	28	16	0
2	28	21	17	18	16	41	23	4

[a] Initial atomic D fraction; f_{D2} = 50.3%, f_{D4} = 0.

significant in Run 2, because the longer hydrogen pretreatment made in Run 2 should have given more hydrogen chemisorbed as demonstrated by the higher conversions of olefins.

In this way, the intermolecular hydrogen transfer disclosed above confirms that both reactions takes place on a common site as expected, being consistent with the alkyl intermediate formed with Co–H;
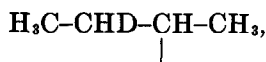
$$Co-H + C_2D_4 \rightarrow Co-D + C_2HD_3,$$
$$Co-D + C_2H_4 \rightarrow Co-H + C_2H_3D,$$

or

$$Co-D + c-C_4H_8 \rightarrow Co-H + 1-C_4H_7D$$

or

$$t-C_4H_7D,$$

where the butyl intermediate would be

$$H_3C-CHD-CH-CH_3,$$

from which either 1-butene or 2-butene may be formed. The 1-butene thus formed should be CH_3—CHD—CH=CH_2, while 2-butene may be either CH_3—CH=CH—CH_3 or

CH_3—CD=CH—CH_3 with about equal probability. Thus 1-butene in the product should contain more d_1 species than trans-butene. This is borne out by the result as shown in Table 2.

3. Relative Rates of Exchange and Isomerization during Competition

The relative magnitude of adsorption strength was qualitatively tested by comparing the competitive rate of reaction with the individual rate, where the catalyst was commonly pretreated with 70 mm Hg of hydrogen at 25°C for 1.5 hr. The results are shown in Table 3, where the rate of reaction is given as the amount of the product formed in the initial 1 min.

It is obvious that the competitive rates of ethylene and butene are significantly reduced from the individual rates, although the extent of reduction is greater for butene than for ethylene. That is, the rate of butene is reduced to $\frac{1}{6}$, while that of ethylene to $\frac{1}{4}$. Thus it follows that the inhibition by ethylene is more significant than that of butene, suggesting a stronger adsorption of ethylene than butene. This

TABLE 3

THE RATE OF C_2H_4–C_2D_4 EXCHANGE AND
cis-BUTENE ISOMERIZATION

Reactants	Exchange (ml stp/min g)	Isomerization (ml stp/min g)
Cis-butene (27 mm Hg)	—	0.15
Cis-butene + mixed ethylene	0.036	0.025
Mixed ethylene (C_2H_4/C_2D_4 = 1, 20 mm Hg)	0.14	—

FIG. 4. Dependence of the initial rate of isomerization of butene pressure.

notion was further examined by changing the olefin ratio.

In such a case, the rates of both reactions are supposed to be proportional to olefin coverage (θ) on active sites, and may be expressed as

$$R_{ex} = k_2 L_H \theta_2$$
$$= k_2 L_H K_2 P_2 / (1 + K_2 P_2 + K_4 P_4), \quad (1)$$

$$R_{iso} = k_4 L_H \theta_4$$
$$= k_4 L_H K_4 P_4 / (1 + K_2 P_2 + K_4 P_4), \quad (2)$$

where L_H is the amount of active hydrogen, P the partial pressure of olefin, k the rate constant, and K the adsorption constant, with subscripts 2 and 4 denoting ethylene and butene, respectively.
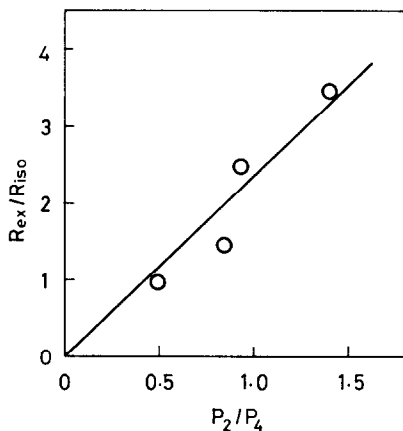

FIG. 3. Competitive reaction of C_2H_4–C_2D_4 exchange and cis-butene isomerization; plot according to Eq. (3).
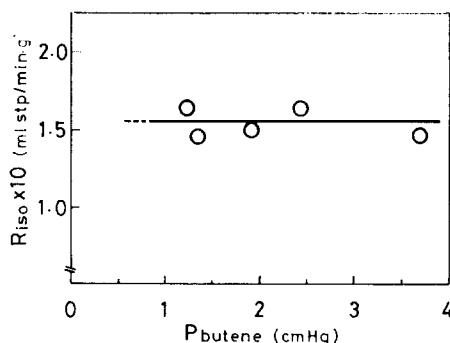
The ratio of initial rates is thus independent of L_H (namely, the time of pretreatment with hydrogen) and is given by

$$R_{ex}/R_{iso} = k_2 K_2 P_2 / k_4 K_4 P_4. \quad (3)$$

By changing the partial pressure of olefins (P_2 = 14–26 mm Hg, P_4 = 19–29 mm Hg), the values of R_{ex}/R_{iso} were determined and are plotted according to Eq. (3) in Fig. 3. There exists a correlation, as expected from Eq. (3), giving the value $k_2 K_2 / k_4 K_4$ = 2.3. If k_2/k_4 is given, the value of K_2/K_4 may be obtained.

In order to estimate the value of k_2/k_4, the kinetics of noncompetitive reaction was examined for the rapid isomerization of butene, where the catalyst was pretreated with hydrogen for 1.5 hr. Figure 4 shows the zero-order dependence of the initial rapid rate of isomerization on butene pressure,[1] suggesting that the active site is fully occupied by butene in the absence of ethylene. Since ethylene appears to be more strongly adsorbed, as indicated from the result of Table 3, one may be allowed to assume the zero-order kinetics for the reaction of ethylene. The zero-order kinetics removes the ambiguity associated with the interpretation of mutual inhibition in the

[1] This does not mean that the rate of disappearance of cis-butene is independent of partial pressure of cis-butene. Rather, it may be approximated to first order with respect to isomeric butene.

competitive reaction. The inhibition must be caused by a decrease in the share of coverage. Thus the zero-order rates may be given by

$$R_{ex} = k_2 L_H, \qquad (4)$$

$$R_{iso} = k_4 L_H. \qquad (5)$$

When L_H is fixed at a certain value by making the hydrogen treatment at a fixed condition, it follows that

$$R_{ex}/R_{iso} = k_2/k_4. \qquad (6)$$

The individual rates of isomerization and isotopic exchange were separately determined for two different treatment times and are tabulated in Table 4. Both values of R/t are nearly the same. The value of k_2/k_4 may be assessed as 0.92 as the average of R_{ex}/R_{iso}. Combining this value with $k_2 K_2/k_4 K_4 = 2.3$ gives the relative adsorption constant: $K_2 : K_4 = 2.5 : 1$.

4. Effect of Prechemisorbed Hydrogen on H_2–D_2 Equilibration

Siegel postulated a "C" site that has three vacant coordination positions and ascribed the H_2–D_2 equilibration to a "CH" site that is formed by the heterolytic splitting of hydrogen on the "C" site. According to this explanation (3), it is expected that the catalyst stabilized with hydrogen treatment, having CH sites, exhibits a higher activity than fresh catalyst for the H_2–D_2 equilibration.

Shigehara and Ozaki (5) have shown that the irreversible adsorption of hydrogen

takes place even at $-195°C$ on the fresh cobalt oxide, and increases with temperature, reducing the molecular and reversible part of hydrogen. MacIver and Tobin (6) have reported that the H_2–D_2 equilibration at $-195°C$ over an oxidized CoO surface that seems to be similar to that of Co_3O_4 is inhibited by the irreversible hydrogen chemisorbed at $-78°C$. In this respect, the effect of temperature of hydrogen pretreatment on the H_2–D_2 equilibration at $-195°C$ was reexamined. The low temperature was chosen to avoid too fast a rate of equilibration. The fresh state of cobalt oxide (4 g) was treated with 21 cm Hg of H_2 for 10 min at each temperature followed by cooling to $-195°C$, at which the gaseous hydrogen was evacuated for 3 min. The activity of fresh catalyst was too high to be determined even at $-195°C$. But after a 10 min treatment with hydrogen at $-195°C$, the rate of reaction could be determined to be 1.0 ml stp/min g. After the hydrogen treatment at -78 and $0°C$, the rates were 0.20, and 0.016 ml stp/min g, respectively. It is clear that the hydrogen treatment gives rise to the striking reduction in the activity. It appears that the chemisorbed hydrogen inhibits the H_2–D_2 equilibration, being contrary to Siegel's expectation (3).

In order to confirm the above result, the effect of hydrogen chemisorption was further examined for the H_2–D_2 equilibration at $-78°C$, where the amount of catalyst was reduced to 0.6 g to make the rate of reaction measurable. At this temperature the rate of exchange could be determined, even with the fresh catalyst, to be 48.3 ml stp/min g under 24 cm Hg. After the first run for 15 min the gases were evacuated for 3 min at the reaction temperature and fresh reactant gases were introduced. The second (for 45 min) and third runs made in this way gave 42.3 and 41.8 ml stp/min g, respectively. Thus the fourth run was made after a contract with the H_2–D_2 mixture (24 cm Hg) at $-78°C$

TABLE 4

The Individual Rate of Isotopic Exchange and Isomerization

Duration of H_2 treatment (t) (hr)	Rate (ml stp/min g)		Rate/t		R_{ex}/R_{iso}
	Ex.	Iso.	Ex.	Iso.	
1.0	0.089	0.097	0.089	0.097	0.92
1.5	0.14	0.15	0.093	0.100	0.93

for 16 hr, giving a rate of 40.7 ml stp/min g. Although the striking reduction in activity as observed at −195°C was not observed at −78°C, there was no indication that the activity is increased by prechemisorption of hydrogen.

In this way, the H_2–D_2 equilibration discloses no positive proof for the existence of the "C" site, at least at −78°C or below.

5. Reexamination of "stabilization" by Hydrogen Treatment

In a previous paper (4) it was stated that "the fresh catalyst is markedly active for the hydrogenation of ethylene in the initial stage of the reaction; however, the activity became lower and lower during the reaction." Thus it was inferred that "the decrease of activity is at least partly caused by the irreversible adsorption of hydrogen." A part of Siegel's proposal for the site of cobalt oxide seems to be based on this statement. However, it was recalled that the statement was based on pressure change measurements. Thus a series of successive hydrogenation runs was made with ethylene over the fresh catalyst. The time courses of ethane formation are shown in Fig. 5, together with the pressure change. As is evident from Fig. 5, the initial rates of ethane formation in each run are nearly the same, whereas the pressure changes are quite different. The rapid pressure change in the initial stage of run 1 is mainly ascribable to the adsorption of ethylene because a comparable amount of irreversibly adsorbed ethylene was detected by the material balance and is shown with the length of arrow in Fig. 5. Thus the notion that the prechemisorbed hydrogen drastically reduces the hydrogenation activity on Co_3O_4 should be abandoned. It seems to block the adsorption site for ethylene, which is ineffective for the hydrogenation, while the hydrogen treatment simultaneously creates the strikingly active site for the alkyl intermediate reactions.
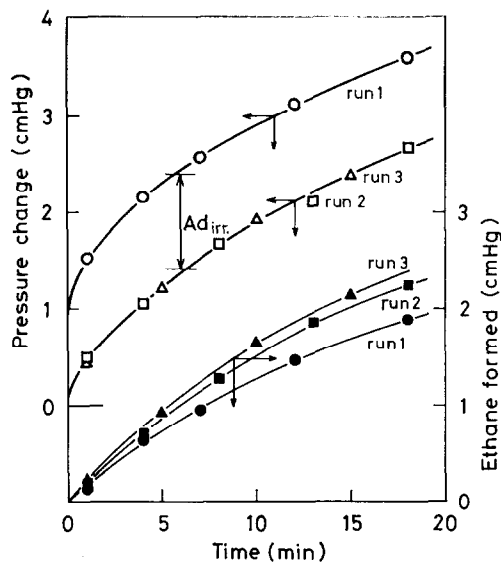

Fig. 5. Time course of ethylene hydrogenation over Co_3O_4 in a series of successive runs.

DISCUSSION

1. The Active Site for the Alkyl Intermediate Reactions

Both the butene isomerization and C_2H_4–C_2D_4 exchange are characterized by the alkyl intermediate, as demonstrated by enhancement with hydrogen (2). The competitive reaction of ethylene and butene with active hydrogen has disclosed that ethylene is more strongly held on the active site than butene. Since this sequence accords with that observed during hydrogenation (1), which is the opposite of that during oxidation (7), the adsorbed state of olefin should be analogous to that during hydrogenation, which was previously concluded to be a π-complex with some electron back donated to olefin. Thus it is very likely that the reacting olefin molecules are adsorbed directly on exposed cobalt ions. On the other hand, the active site should hold the active hydrogen, as demonstrated by the incorporation of prechemisorbed deuterium (2) and by the hydrogen transfer between olefin molecules. It is accordingly concluded that the active site for the butene isomerization as well as the C_2H_4–

C_2D_4 exchange is the exposed cobalt ion to which both a hydride anion and an olefin molecule are simultaneously coordinated as represented by

This is the site BH in Siegel's model of the active site on the oxide surface. Thus the present result seems to support the model as far as the B(BH) site is concerned. The hydrogen enhancement observed for both the isotopic exchange and isomerization can be ascribed to the formation of BH site in the presence of hydrogen.

It should be emphasized that the catalytic activity of cobalt oxide with chemisorbed hydrogen is extraordinarily high. The rate of isomerization was estimated to be 0.63 ml stp/min g, or 1.1×10^{13} molecules/sec cm², which is about two orders of magnitude larger than the specific rate over Al_2O_3 (8) or ZnO (9). The number of active sites as estimated from the number of deuterium atoms incorporated into butane is at most 1×10^{12} sites/cm². On the basis of this value, the turnover number is estimated to be roughly 10 sec⁻¹, which is about two orders of magnitude larger than that determined by Boudart and coworkers for hydrogenation of cyclopropane on platinum catalysts (10).

Although this high activity is lost by the consumption of chemisorbed hydrogen to form butane, the presence of gas phase hydrogen seems to recover it. The previously reported enhancement of isomerization by hydrogen (2) is ascribed to the increase in stationary amount of hydridocobalt species, which is determined by relative rates of hydrogen chemisorption and its consumption to form butane.

2. Siegel's Model of an Active Site

Siegel postulated three types of surface cobalt atom structures A, B, and C accord-

ing to the number of vacant coordination sites 1, 2, and 3, respectively. The structure "A" has been accepted in interpreting catalysis over oxide surface (11), and an evidence for the structure "B" has been obtained in the present study, while no direct evidence has been found for the structure "C."

The structure "C" was postulated by the analogy of homogeneous catalysts and has the merit of giving an explanation for a paired addition of hydrogen to olefin:
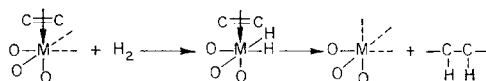
The development of an active site on sulfurated nickel in the presence of acetylene has been explained in terms of the structure "C" (12). Although the attempt to find an evidence for the structure "C" failed in the present study, it still remains likely.

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