JOURNAL OF CATALYSIS 18, 271–280 (1970)

Tracer Study of Ethylene Dimerization over Nickel Oxide–Silica Catalyst

KAZUKO KIMURA, HIDEO A-I, AND ATSUMU OZAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo, Japan

Received December 10, 1969

The role of proton originally held by the catalyst NiO–SiO_2 in the dimerization of ethylene was investigated by means of the deuterium tracer, taking the subsequent isomerization of butene into consideration. It was shown that the deuterium involved in the catalyst did appear in the product butene by way of the isomerization and not of the dimerization. Further study on the dimerization in the presence of C_3D_6 or C_2D_4 revealed that the reacting ethylene molecules rapidly exchange their hydrogen with each other prior to the dimerization. A few micromoles of carbon monoxide adsorbed completely prevented both the isotopic exchange and the dimerization. The mechanism of the dimerization is discussed on the basis of these results. It is suggested that the active site responsible for the dimerization consists of a low valent nickel and an acid.

It has been known that the nickel oxide–silica is an efficient catalyst for the dimerization of lower olefins, particularly of ethylene (*1–4*). This catalyst is also effective for the isomerization of *n*-butene, the mechanism of which has been proved to be a proton donor–acceptor type by means of the deuterium tracer introduced into the catalyst (*5*). Thus it would be expected that the dimerization of ethylene is catalyzed by the acid site. The acidity of the nickel oxide–silica can easily be demonstrated by the color of adsorbed indicator such as dimethyl yellow. Uchida and Imai (*4*) showed that the removal of nickel-containing acid site deactivates the nickel oxide–silica–alumina catalyst for the dimerization.

If the dimerization is catalyzed by the protonic site, the butene molecule formed on deuterated surface is expected to contain deuterium atom in it. This experiment was made previously, and the expectation was fulfilled (*6*). However, in view of the result in the tracer study of the butene isomerization, one must be careful in concluding the intervention of the surface proton in the dimerization. The reactivity sequence of olefins for the dimerization, which was shown by Koizumi (*7*) to be $C_2H_4 > C_3H_6 > C_4H_8$, is unusual for the acid-catalyzed reaction.

Thus it was decided to reexamine the role of acid site in the dimerization in relation to the accompanied isomerization.

EXPERIMENTAL METHODS

Catalysts. The nickel oxide–silica, their numbers, and the procedures of their treatments were the same as employed in the previous study (*5*). The catalysts, NiO–SiO_2-1, -2, and -3 (NS 1, 2, 3) showed a deep black color after calcination at 500°C, and were proved to possess surface protons which are effective for the isomerization of butene, provided that the catalysts were evacuated at around 100°C (*5*). It was also shown that those protons were eliminated by hydrogen treatment at 200°C or by evacuation at higher temperature (*5*).

Reagents. Two kinds of deuteroethylene, A and B, were used. C_2D_4(A) was prepared by exchange reaction between C_2H_4 and D_2O over a platinum–asbestos catalyst, and

TABLE 1

C_2H_4 DIMERIZATION WITH DEUTERATED CATALYSTS AT 0°C

No.	Catalyst NS-	Evacuation temp (°C)	Reaction time (min)	Butene composition			Deuterobutene (%)					F_{D_2}	F_{D_4}	$\frac{F_{D_4}(1\text{-}C'_4)}{F_{D_4}(2\text{-}C'_4)}$
				1-,	*trans*-,	*cis*-,	d_0	d_1	d_2	d_3	d_4			
1	1	70	15	22			77.5	13.2	7.5	1.8	tr.	—	0.22	0.41
					42		47.8	37.3	12.6	1.9	0.4		0.52	
						36	45.3	40.4	11.3	2.4	0.6		0.55	
2	1	70	10	22			84.5	10.6	4.0	0.9	tr.	—	0.16	0.36
					43		56.0	32.3	10.3	1.4	tr.		0.44	
						35	56.1	34.6	8.0	1.3	tr.		0.44	
3	1	100	30	9			74.2	17.1	6.9	1.3	tr.	~0	0.26	0.69
					50		63.3	26.6	7.5	2.6	tr.		0.37	
						41	61.5	26.2	7.2	3.4	1.7		0.39	
4	2	75	7	59			97.6	2.3	0.1	0	0	0	0.02	0.11
					20		82.0	15.9	2.1	tr.	0		0.18	
						22	72.7	25.0	2.3	tr.	0		0.27	
5	3	80	11	69			98.8	1.2	tr.	0	0	—	0.01	0.07
					14		86.1	12.6	1.3	tr.	tr.		0.14	
						16	80.3	18.2	1.5	tr.	tr.		0.20	

6	3	80	11	44			90.0	6.0	4.0	tr.	0		0.10	
					24		57.4	30.6	10.7	1.3	0	—	0.43	0.23
						32	55.1	34.7	9.1	1.1	tr.		0.45	
7	3	80	10	44			94.0	5.0	1.0	tr.	0		0.06	
					24		64.5	28.8	6.3	0.4	0	0	0.36	0.17
						32	64.5	30.4	4.5	0.6	0		0.36	
8	4	100	30	50			100	0	0	0	0	0	0	
					28	22	100	0	0	0	0		0	
9	5	100	30	52			100	0	0	0	0	0	0	
					26	22	100	0	0	0	0		0	
10	1	400	5	3	73	24	100	tr.	0	0	0	—	tr.	
11	3	400	15	14	58	28	100	tr.	0	0	0	—	tr.	
12	4	400	15	42	41	17	100	tr.	0	0	0	—	tr.	
13[a]	1	100	4	50			97.8	2.2	0	0	0	—	0.02	
					30	20	96.8	3.2	tr.	0	0		0.03	
14[a]	2	100	4.5	85			100	tr.	0	0	0	—	tr.	
					7	8	100	tr.	0	0	0		tr.	

[a] Catalysts were pretreated with hydrogen at 200°C.

C_2D_4(B) by deuteration of C_2D_2 over Girdler-58 catalyst. Their isotopic compositions were as follows.

	f_D	d_0	d_1	d_2	d_3	d_4
C_2D_4(A)	0.78	1.0	4.1	16.8	37.7	40.4%
C_2D_4(B)	0.98	—	—	—	8.7	91.3%

where f_D denotes the atomic fraction of deuterium. C_2D_4(B) contained 10% C_2D_6 as the by-product. Two kinds of deuteropropylene, A and C, were used, with the same signs as used in the previous study (*5*). Their f_D values were 0.91 for A and 0.80 for C.

Procedures. The apparatus, the method of reaction and analysis were the same as employed in the previous study (*5*).

RESULTS AND DISCUSSIONS

1. The dimerization of ethylene over the deuterated catalysts. The dimerization of ethylene was carried out on the deuterated catalysts at 0°C for short times. The products were separated by gas chromatography and were subjected to mass spectrometric analyses for their deuterium contents. The results are summarized in Table 1, where F_{D_2} and F_{D_4} denote the mole fractions of deuterospecies in ethylene and butene, respectively. It is shown by Runs 1 to 7 with the catalysts NS-1 to -3 that the deuterium originally involved in the catalysts now appeared in butenes, but not in ethylene. The catalysts were, in these runs, evacuated at 70–100°C for 1 hr after the treatment with heavy water. On the other hand when the catalysts were evacuated at 400°C (Runs, 10 to 12), or pretreated with hydrogen at 200°C to remove the protons effective for the isomerization before the heavy water treatment (Runs 13 and 14), or when the catalysts NS-4 and -5 which had been proved to have no protons effective for the isomerization were used (Runs 8 and 9), no deuterium was found in butene. These features are completely analogous to that found in the isomerization of butene (*5*). Hence those deuterium atoms found in butenes should be examined for where they were picked up.

If the deuterium was picked up in the process of dimerization, the deuterium must be found in the initial product of the dimerization. Since the equilibrium concentration of 1-butene in *n*-butene mixture at 0°C is as low as 1.8%, the result shown in Table 1 indicates that the initial product is 1-butene. In some cases, as shown by the values of F_{D_4} (Runs 1 to 3, 6 and 7), appreciable amounts of deuterospecies were found in 1-butene, whereas much more amounts were in 2-butenes. This increase from 1-butene to 2-butene in F_{D_4} is evidently attributable to the deuterium pickup in the isomerization. The deuterium found in 1-butene also may be attributable to the isomerization, because the backward reaction to 1-butene from 2-butene may give the deuterium to 1-butene.

Indeed, the value of F_{D_4} for 1-butene [$F_{D_4}(1\text{-}C'_4)$] increases with the extent of isomerization to 2-butene. This feature is shown by the plot of the ratio $F_{D_4}(1\text{-}C'_4)$ $F_{D_4}(2\text{-}C'_4)$ against the 2-butene fraction in total butene in Fig. 1, where the results obtained in the isomerization of 1-butene over the same catalysts are quoted from the previous paper (*5*) for comparison. It is obvious that both results from different reactions agree with each other in the value of the ratio $F_{D_4}(1\text{-}C'_4)/F_{D_4}(2\text{-}C'_4)$. This result clearly demonstrates that the deu-

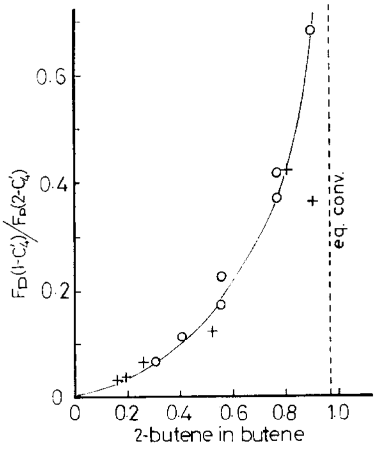

FIG. 1. Variation of D-content in 1-butene [$F_D(1\text{-}C'_4)$] relative to that in 2-butene [$F_D(2\text{-}C'_4)$] with the extent of conversion of 1-butene to 2-butene in the dimerization product (○); and in the isomerization of 1-butene (+).

TABLE 2
EFFECT OF H_2 TREATMENT FOR NS-2 CATALYST

Evacuation temp before the run (°C)	Conversion of $1\text{-}C_4H_8$ to $2\text{-}C_4H_8$ at 25°C, 5 min		Initial rate of dimerization at 25°C (mm Hg/4 min)	
	Untreated	Treated[a]	Untreated	Treated
100	80	27	44	33
200	95	26	39	29

[a] The isomerization activity degraded by the hydrogen treatment was not improved by exposing the treated catalyst to air overnight at room temperature.

terium found in butene was picked up in the process of isomerization and not in the dimerization. It is accordingly concluded that the protonic site originally involved in the catalyst does not participate in the dimerization.

2. The ethylene dimerization in the presence of deuteropropylene. The participation of catalyst proton in the dimerization may be ruled out as described above. However the hydrogen atom originally involved in the reactant might play some role in the dimerization, as found with the butene isomerization over the same catalyst. Thus the dimerization runs were carried out in the presence of deuteropropylene. The black nickel oxide–silica used in these runs had been known to have a protonic acid site which was effective for the isomerization of *n*-butene. In order to minimize the deuterium transfer by way of isomerization, the protonic acid site was eliminated by hydrogen treatment at 200°C. It was previously shown that this treatment completely eliminates the exchangeable hydrogen on the catalyst surface. Other effects of this treatment both on the isomerization and the dimerization are shown in Table 2. It is obvious that the elimination of the protonic site lowers the rate of dimerization, although the effect is less significant than on the isomerization. Hence it appears that the protonic site plays some role in the dimerization, too.

The dimerization of ethylene premixed with C_3D_6 in a C_3/C_2 ratio of 1.26 was carried out at 0°C using the hydrogen-treated catalysts which were evacuated at 100°C before the runs. The resultant mixture was separated by gas chromatography into unreacted ethylene, 1-butene, and 2-butene, the deuterium content of which were analyzed by mass spectrometry. The results are shown in Table 3. It is clear

TABLE 3
C_2H_4 DIMERIZATION IN THE PRESENCE OF C_3D_6

Catalyst	Reaction	$\frac{2\text{-}C'_4}{\text{total } C'_4}$ (%)		D distribution					Atomic fraction f_D
				d_0	d_1	d_2	d_3	d_4–d_8	
NS-2	0°C 4 min	37	C'_2	81.0	15.2	3.2	0.4	0.2	0.056
			$1\text{-}C'_4$	67.0	24.7	6.8	1.3	0.2	0.054
			(calc)	65.5	24.7	7.7	1.0	tr.	
			$2\text{-}C'_4$	63.7	23.3	6.6	2.0	4.4	0.085
NS-5	0°C 7 min	17	C'_2	85.8	13.1	1.1	0	0	0.038
			$1\text{-}C'_4$	73.1	21.8	4.0	1.0	0	0.041
			(calc)	73.6	24.4	3.6	0.3	tr.	
			$2\text{-}C'_4$	68.8	24.1	3.3	1.3	2.5	0.062
NS-2 + CO[a]	0°C; 5 min	—	C'_2	99.1	0.9	0	0	0	0.002

[a] 2.5 μmoles/g of CO was preadsorbed.

that the deuterium formerly involved in propylene now appears in ethylene and butene. Since the atomic fraction of deuterium (f_D) in 1-butene is nearly equal to that of ethylene, it appears that the deuterium first transfers to ethylene prior to the dimerization. The calculated distribution which well agrees with the observed one is obtained assuming a random combination of the recovered deuteroethylene. The higher value of $f_D(2\text{-}C'_4)$ must be due to the isomerization of 1-butene in the presence of C_3D_6 which has been proved to introduce deuterium into butene in the previous study (*5*).

3. Dimerization of light and heavy ethylene mixture. About 1:1 mixtures of C_2H_4 and C_2D_4 (A or B) were dimerized at 0°C for 5 min by the catalysts, NS-2 and NS-5, which were similarly treated at 200°C and then evacuated at 100°C before the runs. The results are shown in Table 4. As indicated by the decrease of d_0 or d_4 and by the increase of d_1–d_3 in the unreacted ethylene, it is evident that ethylene undergoes an isotopic mixing prior to the dimerization. The conversion of ethylene in this mixing may be evaluated from the decrease in the concentration of ethylene-d_0. This amounts to 40 to 44%. On the other hand, in the case of Table 3, the conversion of ethylene was less than 20% under a similar reaction condition. Hence it may be concluded that ethylene reacts faster than propylene in the hydrogen exchange. The difference in the reactivity would be much larger than that indicated by the above values when it is considered that the ratio (C_3D_6/C_2H_4) in the ambient gas mixture increased from the initial value of 1.26 to about 7 during the reaction time of 4 min because of the reactivity difference in the dimerization. Thus ethylene reacts faster than propylene both in the exchange and the dimerization.

Another important result appeared both in Tables 3 and 4 is that a minute amount of carbon monoxide (2.5 μmole/g of cat.) completely prevents the exchange as well as the dimerization. This result suggests both the exchange and the dimerization take place on a same sort of site. Another run was made at 0°C for 5 min measuring the D distribution in butene using NS-2 catalyst pretreated by hydrogen at 200°C. The result is shown in Table 5. The deuterium content in ethylene approximately agrees with that in butene as is the case in the presence of deuteropropylene. However a less satisfactory agreement is found between the observed and calculated D distributions for 1-butene. Since 2-butene in the product amounted to 60%, the isomerization from 1- to 2-butene is likely to have redistributed deuterium atoms, in a similar way as shown in Fig. 1.

4. Isomerization of 1-butene in the presence of deuteroethylene. The isomerization of 1-butene premixed with C_2D_4(B) in a C_2/C_4 ratio of 1.45 was carried out at 0°C. The catalysts NS-2 and -5 were first evacuated at 500°C to remove protonic acid sites effective for the isomerization and then they were preadsorbed with 5.4 and 1.8 μmole/g of carbon monoxide, respectively, to prevent the dimerization of deutero-

TABLE 4

DEUTERIUM DISTRIBUTION IN UNREACTED ETHYLENE IN DIMERIZATION OF C_2H_4–C_2D_4 MIXTURE

C_2D_4	Sample or cat.	D distribution					Atom. fraction
		d_0	d_1	d_2	d_3	d_4	f_D
A	(Reactant)	51.7	2.3	7.3	18.1	20.6	0.39
	NS-2	37.5	21.0	17.6	15.6	8.3	0.34
	NS-2 + CO[a]	52.5	1.5	7.3	17.7	21.0	0.39
B	(Reactant)	49.2	0	0	4.6	48.2	0.50
	NS-2	27.8	18.6	12.4	15.8	25.8	0.48
	NS-5	29.4	17.1	14.2	14.3	25.6	0.47

[a] 2.5 μmole/g of CO was preadsorbed.

TABLE 5

Deuterium Distribution in Unreacted Ethylene and Product Butene in Dimerization of C_2H_4–C_2D_4 Mixture

Sample	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	f_D
Reactant	49.2	0	0	4.6	48.2	—	—	—	—	0.50
Ethylene	31.1	16.7	11.4	14.9	25.9	—	—	—	—	0.47
Butene-1 (40%)	5.2	7.6	11.6	14.8	19.5	17.0	12.4	9.2	3.4	0.51
(calc)	9.4	10.2	9.7	13.7	12.2	11.9	7.9	7.5	6.5	
Butene-2 (60%)	4.7	9.1	12.2	18.1	20.0	15.3	12.1	6.6	1.8	0.47

ethylene, because the formation of deuterobutene should complicate the situation. The results are shown in Table 6, together with a result over a silica–alumina catalyst evacuated at 500°C as reference. The transfer of deuterium from ethylene to butene is obvious, particularly in 2-butene, the product, as shown by the deuterium distribution and by the mole fraction of deuterobutene, F_{D_4}. However these values of F_{D_4} are commonly less than those previously observed in C_3D_6–C_4H_8 system and quoted in the last column of Table 6.

The higher concentration of deuterium in product butene clearly shows that the deuterium originally involved in ethylene is transferred to butene during the isomerization. The mechanism of deuterium transfer was previously proposed as follows:

$$C_nD_{2n} + L^+ \rightarrow C_nD_{2n}L^+, \qquad \text{L, Lewis site,}$$
$$C_2D_{2n}L^+ + C_4H_8 \rightarrow C_2D_{2n-1}L + C_4H_8D^+,$$
$$C_4H_8D^+ + C_2D_{2n-1}L \rightarrow C_2D_{2n-1}HL^+ + C_4H_7D.$$

Since ethylene forms a less stable carbonium ion, it is reasonable on the ground of this mechanism that the deuterium transfer is less extensive in C_2D_4–C_4H_8 than in C_3D_6–C_4H_8. Cationic nature of this transfer is also suggested by the similar result with the well-known acid catalyst silica–alumina.

Accordingly, it may be concluded that the nickel oxide–silica catalyst possesses an acid site which can activate ethylene as carbonium ion and retains this site even after poisoning by carbon monoxide.

5. Acidity of the nickel oxide–silica. Another series of experiments were carried out to study the correlation between acidity and dimerization activity of the catalyst using NS-4. The acidity was measured by *n*-butylamine titration in benzene using dimethyl yellow indicator. The catalyst was pretreated with hydrogen at 200°C to remove dark color of the catalyst. The bright green color thus obtained made the

TABLE 6

Isomerization of 1-Butene in the Presence of C_2D_4 (B) at 0°C

Catalyst	Reaction time (min)	Butene composition (%)		d Distribution				
		1-	2-	d_0	d_1	d_2	F_D	$F_{D\text{-}C_3}$[a]
NS-2 + CO	2	37		97.4	2.6	—	0.03	0.14
5.4 μmole/g			63	89.6	10.4	—	0.10	0.39
NS-5 + CO	25	57		92.3	7.1	0.6	0.08	0.08
1.8 μmole/g			43	82.8	15.3	1.9	0.17	0.38
SiO_2–Al_2O_3	2	58		99.9	0.1	—	0.001	0.03
			42	97.5	2.3	0.3	0.03	0.25

[a] F_D value in the system C_3D_6–C_4H_8, quoted from the previous report (*5*).

titration possible. The catalyst activity for the dimerization was measured by a conventional static method following pressure change, wherein the catalyst was pretreated with hydrogen.

Both results are shown in Fig. 2 as a function of evacuation temperature of the catalyst. As shown in Fig. 2, the dimerization activity increases with the evacuation temperature, except at 100 to 300°C, where the acidity remains constant while the activity decreases. It seems that the increase in the acidity causes the increase in the activity. This is reasonable if the active site for the dimerization involves an acid site, although the acidic nature is not enough to explain the activity.

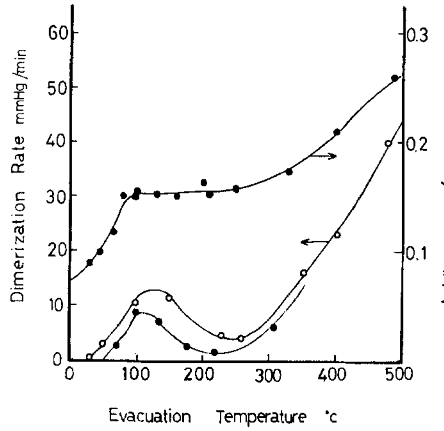

FIG. 2. Variations of acidity and dimerization activity at 25°C with the temperature of evacuation in the pretreatment of the catalyst NS-4.

The nature of acid site measured by the titration was examined by contacting 1-butene with the deuterated catalyst which was prepared by immersing in D_2O overnight followed by evacuation at 100°C. After 1 hr of contact at 100°C only 5 μatom/g catalyst of deuterium was found in butene. This result suggests that large part of the acidity (150 μeq/g of cat.) as measured by the titration may be ascribed to Lewis acid or else they are noneffective for the isomerization of butene.

6. Nature of active site as revealed by poisoning. It was previously reported that nickel oxide–clay catalyst which is similarly effective for the ethylene dimerization is poisoned by (i) carbon monoxide, (ii) water, alcohol, and ether, with fatal amounts being strikingly different between (i) and (ii) (*8*). The circumstance is similar with the present catalyst, nickel oxide–silica as shown in Table 6 for carbon monoxide. It is to be noted, that the carbon monoxide-poisoned catalyst is still effective for the isomerization of butene.

The effects of preadsorbed water on both reactions are shown in Fig. 3, where the activity at 25°C of NS-4 evacuated at 100°C is plotted against the amount of preadsorbed water. As shown in Fig. 3, both activities similarly decrease with increase in the amount of preadsorbed water until 400 μmoles/g of cat. where both reactions are completely prevented. This fatal amount of water, 400 μmoles/g, is in a striking contrast to that of carbon monoxide, 1 to 2 μmoles/g.

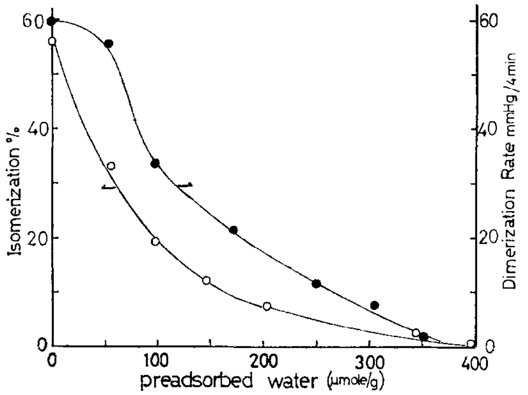

FIG. 3. Variations of rate of dimerization (●); and isomerization (○) with the amount of preadsorbed water.

Since, as previously shown, an acid site is responsible for the isomerization over the present catalyst system, the above result of water poisoning again suggests that an acid site is involved in the active site for the dimerization. However the result of carbon monoxide poisoning suggests another character of the dimerization site because the fatal amount of carbon monoxide is much less than that of water and because the carbon monoxide-poisoned catalyst is still fully active for the isomerization. The dimerization site seems to involve a carbon monoxide-attracting site in addition to the acid site. Generally carbon monoxide is not adsorbed by acid catalysts such as silica–alumina, while strongly adsorbed by transition metals. A number of carbon monoxide complexes are known with zero valent nickel, but none with Ni^{2+} ion. Accordingly the second component of the dimerization site seems to be a low valent nickel atom on the surface.

The nature of this site may be found in nickel oxide which is also effective for the isotopic exchange in ethylene, because both the exchange and the dimerization evidentially take place on a same site over the nickel oxide–silica. It has been reported that the activity for the exchange reaction is developed by dehydration from the nickel oxide surface and is poisoned by carbon monoxide (*9*). Figure 4 shows how the exchange activity of nickel oxide activated at 500°C is decreased by the preadsorbed carbon monoxide. The fatal amount of carbon monoxide corresponds to 0.7 μmole/m². Figure 5 shows that the nickel oxide is activated by evacuation at high temperature for the adsorption of CO and C_2H_4 and that the preadsorbed CO prevents the subsequent adsorption of C_2H_4.

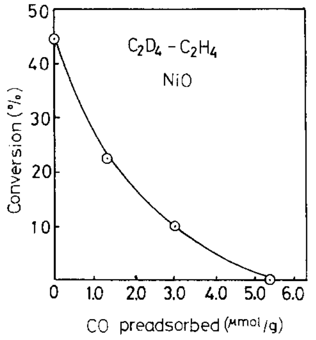

FIG. 4. Effect of preadsorbed carbon monoxide on the extent of isotopic mixing in ethylene at 25°C and 240 mm Hg for 30 min over 1.0 g of nickel oxide activated at 500°C; reactor volume 4.1 ml.

These results indicate that the adsorption site of CO is responsible for the isotopic exchange in ethylene over the nickel oxide.

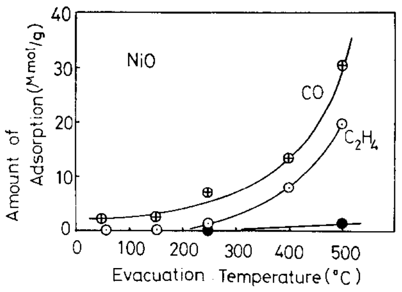

FIG. 5. Effect of evacuation temperature on the amounts of adsorption of carbon monoxide (⊕); and ethylene (⊙) at 25°C and 10^{-1} mm Hg of equilibrium pressure. (●); the ethylene adsorption subsequent to evacuation to 10^{-3} mm Hg of the preadsorbed carbon monoxide.

Since this site of CO adsorption is developed by the evacuation at high temperature and is poisoned by water, it is evidently formed by dehydration from the oxide surface. A further insight into the nature of active site may emerge from an infrared study of adsorbed carbon monoxide. It should be noted at this point that the equilibrium pressure of carbon monoxide is lower than 10^{-1} mm Hg at room temperature on adsorption of the fatal amount of carbon monoxide. Courtois and Teichner observed an absorption band at 1965 cm^{-1} after evacuation of preadsorbed carbon monoxide on nickel oxide, although their sample was prepared by decomposing nickel hydroxide at 200°C *in vacuo*. Similar bands at 1985 and 1925 cm^{-1} were observed by Alexeyev and Terenin for the adsorption of carbon monoxide (20 cm Hg) on nickel oxide evacuated at 400°C. Such an absorption band near 1940 cm^{-1} is also found for the adsorbed carbon monoxide on nickel metal and is clearly different from that of adsorbed carbon dioxide. These results suggest the low valent nature of the nickel atom responsible for the carbon monoxide adsorption. Although the process of formation of the low valent nickel is not clear yet, it seems that the oxygen vacancy caused by the dehydration from the surface is responsible for the exchange reaction. The dimerization of ethylene seems to be effected by cooperation of the low valent nickel with the acid site.

7. Possible mechanism of the dimerization. As is clear from the comparison of ethylene molecule with its initial dimerization product, 1-butene, this reaction involves a hydrogen transfer between reacting ethylene molecules. The nature of the dimerization may be reduced to the nature of this transfer. The result obtained in this study suggests that the transfer by way of proton originally involved in the catalyst may be ruled out. The rapid isotopic mixing found in the unreacted ethylene strongly suggests that the hydrogen transfer is taking place prior to the rate determining step of the dimerization without participation of foreign hydrogen. Such an isotopic mixing must be initiated by dissociative adsorption of ethylene $C_2H_4 \rightarrow C_2H_3(a) + H(a)$ followed by the exchange reaction

$$C_2D_4 + H(a) \rightarrow C_2HD_4(a) \rightarrow C_2HD_3 + D(a),$$
$$C_2H_3(a) + D(a) \rightarrow C_2H_3D.$$

Thus there must be an adsorbed ethyl species of short lifetime on the catalyst surface during the reaction.

The dimerization may be effected by an insertion of ethylene molecule into the adsorption bond on the ethyl species followed by elimination of secondary hydrogen, or otherwise by reaction of the ethyl with the vinyl group which is formed in the dissociative adsorption of ethylene. Since nickel oxide itself is only effective for the isotopic mixing and not for the dimerization, the latter possibility is unlikely. It seems that the ethyl species formed on the nickel containing site of the nickel oxide–silica is attacked by ethylene activated by acid part of the active site, whereas the attacking ethylene must be equilibrated with other adsorbed species in its isotopic composition.

A completely different scheme for the dimerization has been proposed by Imai *et al.* (*10*) on the basis of product distribution in the dimerization of propylene over $NiO–SiO_2–Al_2O_3$ at 100 and 200°C. They adopted a cyclobutane intermediate to explain the initial formation of 2-hexene, 3- and 4-methylpentene, and 2,3-dimethylbutene from propylene, which is in marked contrast to the present result of 1-butene from ethylene. The reason for the difference is not clear, but seems to arise from the presence of alumina, and the higher reaction temperature.

Finally the proposed mechanism should be consistent with the characteristic feature of the dimerization over nickel oxide–silica that ethylene is more reactive than propylene. This reactivity sequence seems reasonable on the ground of the present mechanism in view of the relative ease in the dissociation of C–H bond of double-bonded carbon which is required as an initial step of the reaction in the proposed mechanism. A steric effect of alkyl group in the insertion step may also be possible.

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