

Catalysis and Coordinative Unsaturation of Active Sites on Sulfurated Nickel Catalyst¹

II. Catalytic Activity and the Degree of Coordinative Unsaturation of Active Sites

ATSUSHI TAKEUCHI, KEN-ICHI TANAKA AND KOSHIRO MIYAHARA

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

Received March 5, 1975

Sulfurated nickel prepared from nickel wire by contacting with H₂S at 300°C is inactive for hydrogenation of acetylene, ethylene and butene, hydrogen exchange reactions of H₂-D₂, H₂-C₂D₄ and D₂-C₂H₈, and dimerization of acetylene, however, it becomes active for isomerization of butene and C₂H₄-C₂D₄ exchange reaction in coexistence of hydrogen. In contact with acetylene for several hours, this catalyst surface becomes active for the above hydrogenations as well as for H₂-D₂ equilibration, but its catalytic activities vanish reversibly by removing acetylene. These characteristics of the sulfurated nickel catalyst are well understood on the basis of the degree of coordinative unsaturation of surface nickel atoms as proposed by Siegel [*J. Catal.* 30, 139 (1973)] with respect to some oxide catalysts.

INTRODUCTION

In the preceding paper (1), the authors obtained some experimental evidences suggesting reversible formation of active sites for hydrogenation of acetylene and olefins and H₂-D₂ equilibration reaction on sulfurated nickel in contact with acetylene.

In this paper the nature of active sites was investigated systematically by using a series of reactions; hydrogenation of a mixture of C₂H₂ and C₂D₂, hydrogen exchange reactions of C₂H₄-C₂D₄, H₂-C₂D₄ and D₂-C₄H₈, and isomerization of butene. As discussed in this paper, the catalytic activity and the selectivity of the sulfurated nickel are well understood on the idea of the degree of coordinative unsaturation of surface nickel atoms (2) having been established in the metal complex catalyst (3,4).

¹ Abstracted in part from the doctoral thesis of A. Takeuchi, Hokkaido University.

EXPERIMENTAL METHODS

The reactions were carried out in a system used in the previous works (1,5). Nickel wire (Toshiba Elect. Co.) of 0.1 mm in diameter and 120-140 m in length was sulfurated with hydrogen sulfide at 300°C (1).

C₂D₂ prepared by reaction of calcium carbide with D₂O was purified by distillation *in vacuo*. C₂D₄ was prepared by deuteration of C₂D₂ over palladium-asbestos and was purified by contacting with silica gel to remove a trace of acetylene. Hydrogen and deuterium were purified through palladium-silver thimbles.

Analysis of hydrocarbons was carried out by a gas chromatograph as described in the previous papers (1,5). H₂, HD and D₂ were analyzed by a mass spectrometer at 70 V of ionization voltage and deuterated ethylene and butenes were analyzed at 12.5 V. In the case of co-hydrogenation of C₂H₂ and C₂D₂, deuterated C₂ species were analyzed by a gaschromatography-mass spec-

trometer at 70 V equipped with a silica gel column.

RESULTS

Isomerization of Butene

When 1-butene alone is contacted with surface I, i.e., freshly sulfurated nickel (I), neither the isomerization of butene nor the self-hydrogenation of butene were observed in 5.8 hr at 120°C. However, if a mixture of hydrogen and 1-butene is admitted at 121°C, the isomerization of butene takes place as shown in Fig. 1a accompanying no induction period in contrast with the hydrogenation of acetylene (I).

Hydrogenation of butene to *n*-butane being only 1.7% in 6.1 hr at 121°C is negligibly slow compared with its isomerization.

In order to elucidate a question whether the catalyst surface during the isomerization remains to be surface I or not, the ambient gas was quickly removed on the way of the isomerization by evacuation for 2 min at 121°C and the hydrogenation of acetylene was followed on the same catalyst. An apparent induction period characterizing the surface I was observed as

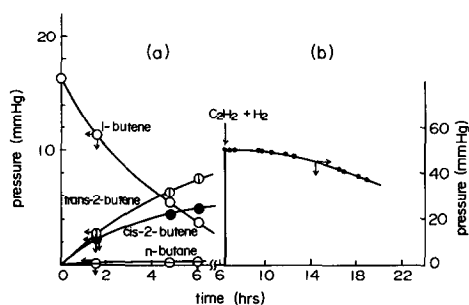


FIG. 1. (a) Isomerization of 1-butene over sulfurated nickel at 121°C in coexistence of H_2 . Initial pressures are 1-butene = 16.3 mm Hg and H_2 = 32.9 mm Hg. (b) Hydrogenation of acetylene on the same catalyst at 121°C after the reaction of (a). Initial pressures are C_2H_2 = 17.0 mm Hg and H_2 = 33.2 mm Hg.

shown in Fig. 1b. The surface I contacted with hydrogen, denoted as surface I- H_2 , undoubtedly promotes the isomerization of butene but no hydrogenation.

In order to clarify the role of hydrogen, isomerization of 1-butene (19.7 mm Hg) was carried out in the coexistence of deuterium (137.9 mm Hg containing 1.2% of HD) over surface I at 121°C. The composition of butene isomers and the deuterium distribution in the whole butene are listed in Table 1. It is evident that isotopic mixing between hydrogen and butene is far slower than the isomerization and that the

TABLE 1
ISOMERIZATION OF 1-BUTENE (%) IN COEXISTENCE OF D_2 AND THEIR ISOTOPIC MIXING

Time (hr):	1.4	3.1	5.7	7.4	Equilibrium
1-Butene	75.6	60.8	44.5	36.8	(7.7)
<i>trans</i> -2-Butene	13.4	21.9	32.8	38.4	(63.9)
<i>cis</i> -2-Butene	11.0	17.3	22.7	24.8	(28.4)
Butene- d_0	97.0	93.9	91.2	89.6	
- d_1	3.0	5.4	8.0	9.4	
- d_2	0	0.7	0.8	1.0	
- d_3	0	0	0	0	
Av. D content (%)	0.4	0.9	1.2	1.4	
H_2	0.3	0.9	1.4	1.6	
HD	1.4	1.8	2.1	2.3	
D_2	98.3	97.3	96.5	96.1	

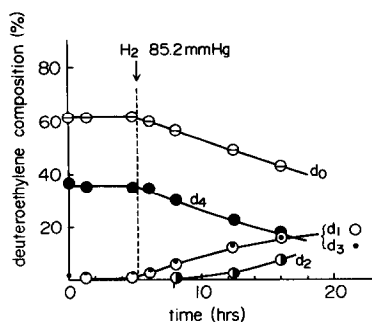


FIG. 2. Acceleration of $C_2H_4-C_2D_4$ exchange by hydrogen addition over sulfated nickel at $121^\circ C$. Initial pressure is 41.1 mm Hg ethylene ($-d_0$, 61.5%; $-d_3$, 1.7%; and $-d_4$ 36.8%). H_2 is added at 5.2 hr.

hydrogenation of butene is also so slow to give only 0.6% of butene consumption in 7.4 hr.

Hydrogen Exchange between C_2H_4 and C_2D_4

Isotopic mixing between C_2H_4 and C_2D_4 did not take place appreciably over surface I but was accelerated obviously by adding hydrogen as shown in Fig. 2, indicating surface I- H_2 is active for this isotopic exchange reaction. In this reaction the isotopic mixing between the added hydrogen and ethylene as well as the hydrogenation of ethylene are negligibly slight as shown in Table 2, being quite similar to the butene isomerization.

Co-hydrogenation of C_2H_2 and C_2D_2

Hydrogenation of a mixture of C_2H_2 and C_2D_2 was carried out over surface I, and the time courses of the total pressure change and the HD formation are shown in Fig. 3. The surface I became active for

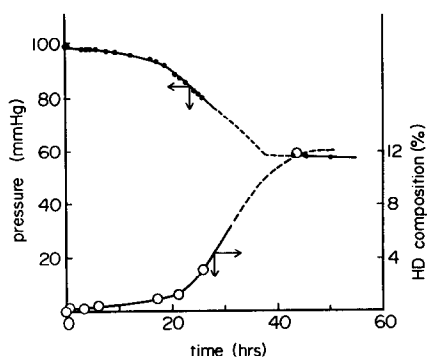


FIG. 3. Hydrogenation of $C_2H_2-C_2D_2$ mixture with H_2 over sulfated nickel at $121^\circ C$. Initial pressures are $C_2H_2 = 34.2$ mm Hg and $H_2 = 64.5$ mm Hg.

both the reactions after induction periods of about 20 hr, and the activated surface was named surface II (I).

Deuterium distribution in acetylene, ethylene and hydrogen is summarized in Table 3. The isotopic mixing between C_2H_2 and C_2D_2 was very slow as well as between acetylene and H_2 on both surface I and surface II.

The isotopic ethylenes were mainly ethylene- d_0 , $-d_1$ and $-d_2$, distinctly differing from the random distribution of D atoms, but they approached to the random one at 43.2 hr.

DISCUSSION

The selective partial hydrogenation of acetylene on metal catalysts has been usually explained by the relative adsorption strength in the order of $C_2H_2 > C_2H_4 > C_2H_6$ or by the relative rates of $C_2H_4(a) \rightarrow C_2H_4$ and $C_2H_4(a) + H_2 \rightarrow C_2H_6$, as being named as thermodynamic and mechanistic factor (5), respectively, where (a) denotes an adsorbed state.

TABLE 2
CHANGE OF ISOTOPE COMPOSITION (%) OF HYDROGEN DURING THE $C_2H_4-C_2D_4$ EXCHANGE IN COEXISTENCE OF H_2

Time (hr):	5.2	6.1	8.1	12.4	16.0
H_2	100.0	99.4	98.7	98.6	98.4
HD	0	0.6	1.0	1.2	1.4
D_2	0	0	0.3	0.2	0.2

TABLE 3
DEUTERIUM DISTRIBUTION (%) IN PRODUCTS OF HYDROGENATION OF
C₂H₂-C₂D₂ MIXTURE WITH H₂

Time (hr):	0	0.7	3.3	6.0	17.4	21.2	25.9	43.2
Acetylene- <i>d</i> ₂	52.5	49.0	55.4	52.0	51.1	49.9	48.7	—
- <i>d</i> ₁	1.9	5.0	4.9	4.5	6.3	6.6	7.4	—
- <i>d</i> ₀	45.6	46.0	39.7	43.5	42.6	43.5	44.0	—
Av. D content (%)	53.5	51.5	57.9	54.3	54.3	53.2	52.4	—
H ₂	100	99.6	99.7	99.6	99.0	98.6	96.5	87.2
HD	0	0.2	0.2	0.3	0.9	1.2	3.1	11.8
D ₂	0	0.2	0.1	0.1	0.1	0.2	0.4	1.0
Ethylene- <i>d</i> ₄						0.4	0.3	0.5 (0.5) ^a
- <i>d</i> ₃						5.3	5.6	5.4 (5.6)
- <i>d</i> ₂						32.7	32.0	28.7 (23.0)
- <i>d</i> ₁						24.1	25.8	31.3 (42.0)
- <i>d</i> ₀						37.5	36.3	34.1 (28.9)
Av. D content (%)						26.8	27.0	26.7

^a Parentheses show the random distribution at 26.7% of D content.

On the other hand, in the catalytic hydrogenation with metal complexes, the degree of coordinative unsaturation of central metal atom or ion and the coordination of hydrogen atoms, that is, a structural factor of active sites is the most important factor to control the catalytic activity and/or the selectivity. Some typical cases have been observed on RhCl(PPh₃)₃ (I), RhH(CO)(PPh₃)₃ (II) and IrCl(CO)(PPh)₂ (III); complex (I) catalyzes the hydrogenation of alkenes but not the H₂-D₂ equilibration reaction, while (II) is active for both the reactions and (III) is less active than (I) and (II) for the hydrogenation due to difficulty of ligand dissociation. These specific properties have been well explained by the degree of coordinative unsaturation of central metal (3,4).

The present experiments on the sulfurated nickel demonstrate that the catalytic activity and/or the selectivity for the series of reactions are controlled by reversible change of coordinative unsaturation of surface nickel atoms in cooperation with acetylene adsorption (1), and

the resulting specific properties are closely related to the model proposed by Siegel (6) for the specific catalysis of oxides (7).

The C₂H₄-C₂D₄ exchange reaction and isomerization of butene occur on freshly sulfurated nickel under coexistence of hydrogen (surface I-H₂) but hydrogenation of olefin hardly proceeds. Surface I or I-H₂ changes to surface II with a long induction period in contact with acetylene, on which the H₂-D₂ equilibration and the hydrogenation of acetylene as well as olefins (1) can take place. Catalytic activities of surface I and II for the series of reactions are showed collectively in Table 4.

As shown in the preceding paper (1) the sulfurated nickel surface has a ratio of S/Ni = 0.69, being quite similar to nickel subsulfide Ni₃S₂. Taking into account that nickel atom in Ni₃S₂ is surrounded by four sulfur atoms and by six sulfur atoms in NiS, the degree of coordinative unsaturation of nickel atoms in NiS is supposed to be zero and in Ni₃S₂ is two, which may infer the degree of coordinative unsaturation of the surface I.

TABLE 4
 CATALYTIC ACTIVITIES OF SULFURATED NICKEL^a

Reactions	Surface		
	(I)	(I-H ₂)	(II)
Isomerization of butene	-	+	
Exchange of C ₂ H ₄ -C ₂ D ₄	-	+	
Hydrogenation of C ₂ H ₂		-	+
Hydrogenation of C ₂ H ₄ or C ₄ H ₈		-	+
Exchange of H ₂ -D ₂		-	+
Exchange of H ₂ -C ₂ D ₄ , D ₂ -C ₄ H ₈		-	+
Dimerization of C ₂ H ₂	-	-	+

^a + active; - inactive.

The active sites having 1, 2 and 3 degrees of coordinative unsaturation are denoted as type A, type B and type C (Fig. 4), respectively, according to Siegel (6). The C₂H₄-C₂D₄ exchange taking place on surface I-H₂ is well understood by regarding BH sites on surface I-H₂. That is, B sites on surface I may change to BH by process (1), i.e., heterolytic chemisorption of hydrogen (Fig. 5). The C₂H₄-C₂D₄ exchange is promoted on site BH according to the forward and backward processes of process (2). Isomerization of butene can take place on surface I-H₂ through process (2) via similar, half-hydrogenated intermediate.

Homolytic chemisorption of hydrogen on a nickel atom of site B may also be considered in addition to process (1), however, it cannot contribute to H₂-D₂ equilibrium reaction, C₂H₄-C₂D₄ exchange and isomerization of butene, because there is no vacant site for coordination of another molecule on nickel atom. The reverse of process (1) is concluded to be negligibly slow at about 120°C, because H₂-C₂D₄ exchange and D₂-C₄H₈ exchange during C₂H₄-C₂D₄ exchange and

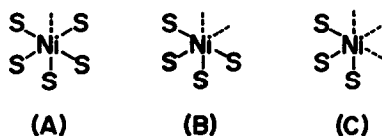


FIGURE 4.

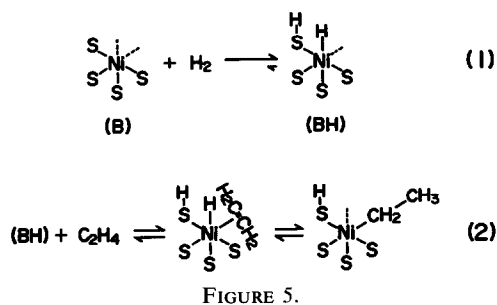


FIGURE 5.

isomerization of butene are very slow, as shown in Tables 1 and 2.

Consequently, hydrogen atom coordinated on nickel atom is used repeatedly in process (2) with few consumed by hydrogenation or by the reverse of process (1), in another word, it acts as a kind of cocatalyst. A similar behavior of hydrogen is observed with the C₂H₄-C₂D₄ exchange catalyzed by metal complex Ni(PPh₃)₂X₂, where hydrogen markedly accelerates the exchange but isotopic mixing between hydrogen and ethylene is very slow (8).

The fact that surface I is inactive for C₂H₄-C₂D₄ exchange and isomerization of butene indicates few hydrogens from H₂S remain over surface I, that is, the heterolytic adsorption of hydrogen may become reversible at such a high temperature as 300°C.

Catalytic activities of surface II are well understood with type C sites. Hydrogenation of olefin and acetylene as well as H₂-D₂ equilibration can proceed on site C and/or CH as shown in Fig. 6.

Mechanism of hydrogenation given by processes (3) and (4) are similar to those proposed on metal complex (I) and (II), respectively, and the mechanism of H₂-D₂ equilibration given by process (5) is similar to that proposed on metal complex (II).

From these reaction schemes the hydrogenation of olefin (or acetylene) cannot proceed on sites B and BH, since olefin (or acetylene) and two hydrogen atoms cannot coordinate simultaneously on a nickel atom.

The change of surface I to surface II in

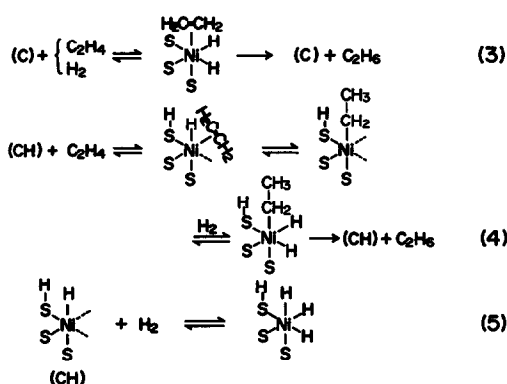


FIGURE 6.

contact with acetylene reveals the formation of sites C by removing one sulfur atom of site B to another site B, that is, $2B \rightleftharpoons A + C$. When acetylene is exhausted by hydrogenation or by trapping, backward process recovering two B sites makes the surface inactive for hydrogenation. This slow surface migration of sulfur is observed as an induction period in acetylene hydrogenation and as a deactivation of surface II for the hydrogenation of produced ethylene as well as for H_2 - D_2 equilibration (1).

The adsorption of acetylene on surface I- H_2 and on surface II is irreversible as revealed by the absence of C_2H_2 - C_2D_2 exchange product in Table 3. On the contrary, ethylene adsorbs reversibly on surface I- H_2 but is unable to generate surface II. A sequence of coordination strength on nickel atom is, thus, concluded to be $C_2H_2 > S > C_2H_4$.

In conclusion, the characteristic catalytic activity and/or selectivity of sulfurated nickel are well understood by the change of degree of unsaturation of surface nickel atom by coordinative sulfur. The type of active sites mentioned above are substantially in agreement with Siegel's model (6). In the present case sites B and C, namely surface I and II, are realized individually by their distinct selectivity in catalysis.

A peculiar exchange between deuterium

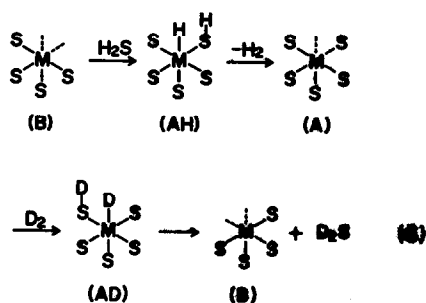
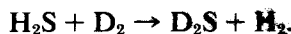


FIGURE 7.

and hydrogen sulfide, keeping molecular identity, has been found at about $500^\circ C$ over the various sulfides such as silver, manganese, iron, copper and molybdenum (9);



However, the mechanism explaining this exchange has not been settled up. Decomposition of hydrogen sulfide is known to be in equilibrium at about $500^\circ C$ but the isotopic mixing is very slow. Regarding the surface contacting with H_2S has either type A or type B sites, the isotopic mixing is unable to proceed according to the present model (Fig. 7). As mentioned above, heterolytic adsorption of hydrogen is reversible at a temperature as high as $500^\circ C$, however, strong adsorption of H_2S on B sites suggests that the surface during reaction is constructed by A type sites, on which H_2 - D_2 equilibration is prohibited.

These results may allow us to derive a conclusion that activity and selectivity for solid catalysts, e.g., oxides, sulfides and halides, etc., of transition metals, may be controlled not only by the thermodynamic and mechanistic factors, but also by a structural factor of active sites, i.e., the degree of coordinative unsaturation and coordination of hydrogen atom onto metal atom, similarly to catalysis by transition metal complexes.

REFERENCES

1. Takeuchi, A., Tanaka, K., Toyoshima, I., and Miyahara, K., *J. Catal.* **40**, 94 (1975).

2. Takeuchi, A., Tanaka, K., and Miyahara, K., *Chem. Lett.* (The Chemical Society of Japan), 171, 411 (1974).
3. Osborn, J. A., Jardine, F. H., Young, J. F., and Wilkinson, G., *J. Chem. Soc. A* 1711 (1966); Jardine, F. H., Osborn, J. A., and Wilkinson, G., *J. Chem. Soc. A* 1574 (1967); Evans, D., Yagupsky, G., and Wilkinson, G., *J. Chem. Soc. A* 2660 (1968); O'Connor, C., and Wilkinson, G., *J. Chem. Soc. A* 2665 (1968); Siegel, S., and Ohrt, D. W., *Inorg. Nucl. Chem. Lett.* **8**, 15 (1972); Halpern, J., and Wong, C. S., *J. Chem. Soc. Chem. Commun.* 629 (1973).
4. Collman, J. P., *Trans. N.Y. Acad. Sci.* **30**, 479 (1968); Collman, J. P., *Accounts Chem. Res.* **1**, 136 (1968).
5. Takeuchi, A., and Miyahara, K., *J. Res. Inst. Catal., Hokkaido Univ.* **21**, 132 (1973); Sheridan, J., *J. Chem. Soc.* 133 (1945); Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
6. Siegel, S., *J. Catal.* **30**, 139 (1973).
7. Tanaka, K., Nihira, H., and Ozaki, A., *J. Phys. Chem.* **74**, 4510 (1970).
8. Ando, N., Maruya, K., Mizoroki, T., and Ozaki, A., *J. Catal.* **20**, 299 (1971).
9. Fueki, K., Inaba, H., and Mukaibo, T., *Bull. Chem. Soc. Jap.* **43**, 23 (1970); Katsumoto, M., Fueki, K., and Mukaibo, T., *Bull. Chem. Soc. Jap.* **46**, 1624, 3641 (1973); Katsumoto, M., Fueki, K., and Mukaibo, T., *Bull. Chem. Soc. Jap.* **47**, 54 (1974).