Catalysis and Coordinative Unsaturation of Active Sites on Sulfurated Nickel Catalyst[1]

I. Reversible Formation of Active Sites for Partial Hydrogenation of Acetylene

ATSUSHI TAKEUCHI, KEN-ICHI TANAKA, ISAMU TOYOSHIMA
AND KOSHIRO MIYAHARA

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

Active sites are generated on sulfurated nickel surface by contacting with acetylene, on which the hydrogenation of acetylene and ethylene as well as the H_2–D_2 equilibration reaction proceed. These sites are wiped up by exhaustion of acetylene, and such reversible formation and vanishment of the active sites controls the partial hydrogenation of acetylene to ethylene on the sulfurated nickel catalyst. A nickel sulfide having an atomic ratio of $S/Ni = 0.62$ had the activity for the partial hydrogenation of acetylene, while a nickel sulfide of $S/Ni = 0.96$ had no catalytic activity. The surface composition of the sulfurated nickel estimated by Auger electron spectroscopy was a value of the ratio $S/Ni = 0.69$.

From these results it is concluded that partial hydrogenation is enabled by reversible formation of active sites on sulfide with appropriate coordinative unsaturation of nickel atoms.

INTRODUCTION

Modification of nickel catalyst with chalcogen such as sulfur and selenium, and with halogen enhances the catalytic selectivity for partial hydrogenation of acetylene to ethylene (*1*), and similar selective partial hydrogenation of polyolefins over sulfurated nickel and nickel sulfide have been reported; selective hydrogenation of isoprene to methyl-butenes (*2*) and cyclic polyenes to corresponding cyclic monoolefins (*3*) over sulfurated nickel, partial hydrogenation of 4-vinylcyclohexene on nickel subsulfide Ni_3S_2 (*4*). Partial hydrogenation of polyenes to corresponding monoolefins was found to take place on nickel sulfide NiS (*5*), however, it was found to be Ni_3S_2 under its working state (*6*).

It is interesting to throw light on the role of sulfur in the selective partial hydrogena-

tions. This paper gives the evidences for reversible formation of active sites for hydrogenation on sulfurated nickel by contact with acetylene (*7,8*). Surface composition of sulfurated nickel was estimated by Auger electron spectroscopy (AES). And the catalytic activity and selectivity of sulfurated nickel are well understood by the coordinative unsaturation of surface nickel atoms (*8*).

EXPERIMENTAL METHODS

Reactions were carried out in a conventional, closed circulation system similar to the previous one (*9*) with a volume of 600 ml and the circulating velocity of about 1700 ml/min. Hydrogen or deuterium was purified by diffusing a palladium–silver thimble. High purity carbon monoxide and oxygen (Takachiho Chem. Co.) were used without further purification and acetylene (Takachiho Chem. Co.) was purified by distillation *in vacuo*.

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

Analysis of reacting gases were carried out by a gas chromatograph with a silica gel column for methane, ethane, ethylene and acetylene, and with a VZ-7 column (Gaschro Industrial Co.) for propylene, isomers of butene, 1,3-butadiene and n-butane. Deuterated hydrocarbons and hydrogen were analyzed with a mass spectrometer (Hitachi RMU-6). Ethylene was analyzed at 13 V of the ionization voltage, while hydrogen at 70 V. Acetylene and ethane were analyzed with gaschro-mass spectrometer with a silica gel column at 70 V of the ionization voltage.

Nickel wires (Toshiba Electric Co.) of 0.1 mm in diameter and of 210 m (Fig. 1), 130 m (Fig. 3) or 160 m (Fig. 4) in length were used as catalyst. Nickel wire mounted in a reactor was heated preliminarily in 1 mm Hg oxygen at 500°C for 5 min and reduced with hydrogen of 60 mm Hg at 500°C for 1 hr. The wire was oxidized again in 1 mm Hg oxygen at 500°C for 5 min and reduced with hydrogen of few tens mm Hg at 300°C for 10 hr, and finally evacuated for 2 hr at 300°C.

As the catalytic properties of sulfurated metals depend on the sulfur compound used, duration and temperature of sulfuration (2,3,5), sulfuration in this work was carried out by hydrogen sulfide to exclude deposition of carbon compounds on the surface of catalyst. Hydrogen sulfide of 0.8–1.1 mm Hg was completely decomposed on nickel catalyst at 300°C for 2 min. After evacuation of evolved hydrogen for 4 min at 300°C, the reactor was cooled to reaction temperature. Amount of sulfur deposited on nickel is much more than monolayer and the atomic ratio (S/Ni) of deposited sulfur to total nickel of wire is about 10^{-4}.

In order to compare the catalytic properties of sulfurated nickel, nickel sulfides having S/Ni ratio of 0.02, 0.62 and 0.96 were prepared as follows. Nickel oxide of about 0.5 g prepared by pyrolysis of nickel carbonate (special grade from Koso Chem.

Co.) at 500°C in air was reduced with hydrogen at 350°C for 100 hr in a reactor, and nickel powder obtained was sulfurated with hydrogen sulfide at 300°C. The rate of sulfuration became very slow at S/Ni approached to 1.0 and the amount of hydrogen sulfide reacted with nickel powder was estimated from the amount of remaining hydrogen sulfide condensed into liquid nitrogen trap.

By using a nickel plate of $1 \times 10 \times 10$ mm^3 (Toshiba Elec. Co.), surface composition of the sulfurated nickel was examined by Varian 981-1000 analytical Auger spectrometer, of which the primary electron was 1.5 keV. The base pressure of the system was of the order of 10^{-8} mm Hg. None of metals other than nickel was detected by the AES analysis of the nickel plate and wire used in this work.

NiS powder of 99.9% purity (Yamanaka chemical Industrial Co.) was disked by a pressure of 560 kg/cm^2 and adopted as a standard sample for AES analysis.

In AES analysis, the sample was set in the AES apparatus in air and after evacuation at a room temperature differential energy distribution $dN(E)/dE$ was recorded vs Auger electron energy E. Table 1 shows the peak positions of respective elements, which are assigned by energy at the high-energy minimum in differential energy distribution curve (10).

In order to estimate the penetration of sulfur in bulk, the plate sample was sputtered by argon ions (600 eV) at a pressure of 5×10^{-5} mm Hg. The change of peak-

TABLE 1
AUGER PEAK POSITIONS

Element	Energy (eV)	Transition
Ni	783	LMM
	61	MMM
O	510	KLL
C	272	KLL
S	152	LMM

peak amplitudes of differential curve was plotted as a function of sputtered depth estimated by number of argon ions, N_{ion}, bomberded per unit surface area of sample which is given by

$$N_{ion} = \frac{I_A \times t}{1.6 \times 10^{-19}},$$

where I_A is a current density and t is a duration of argon ion bombardment. Number of sputtered atoms from the sample, N_{atom}, is given by $Y \times N_{ion}$ where Y is sputtering yield. If one assumes 10^{15} atoms/cm^2 on sample surface, number of sputtered layers is given by $N_{atom}/10^{15}$, and the sputtered depth (Å) is given by a following equation:

$$L = \frac{a \times I_A \times Y \times t}{1.6 \times 10^{-4}},$$

where a is the lattice constant of sample. In this case I_A was 4.8 μA/cm^2 and a and Y are approximated with those of nickel, $a = 3.2$ Å and $Y = 1.2$ (11).

RESULTS AND DISCUSSION

Typical time course of acetylene hydrogenation on freshly prepared sulfurated nickel is shown in Fig. 1 with solid lines. The freshly sulfurated surface becomes active for hydrogenation of acetylene after an induction period of several hours. The
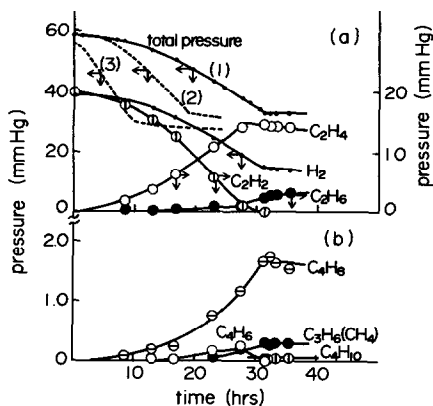
simultaneous dimerization reaction also has the same induction period and 1,3-butadiene formed is hydrogenated to butene during hydrogenation of acetylene. Consecutive hydrogenation of produced ethylene and butene are very slow even after the exhaustion of acetylene in contrast with nickel catalyst, over which olefin is successively hydrogenated as soon as acetylene is exhausted ($9,13$).

Even though the rate of acetylene hydrogenation on sulfurated nickel is less than one tenth of that of nickel, distribution of products during acetylene hydrogenation is nearly the same on nickel and sulfurated nickel as illustrated in Fig. 2. Selectivity S_2 is a ratio of ethylene and ethane (C_2) to the total amount of consumed acetylene, and selectivity S_E is a percentage of ethylene in C_2 products (9). This result suggests that active sites for hydrogenation of acetylene and its dimerization on nickel and sulfurated nickel are commonly nickel atoms and sulfur retards the consecutive hydrogenation of produced monoolefins.

After the first run of Fig. 1, run 2 (broken curve) was carried out on the sulfurated nickel which was treated with 30 mm Hg hydrogen at 300°C for 18 hr and evacuated. After run 2, catalyst was kept at room temperature in contact with reacted gas for more than 1 wk and run 3 was started after degassing at 119°C. Induction period is shortened and catalytic
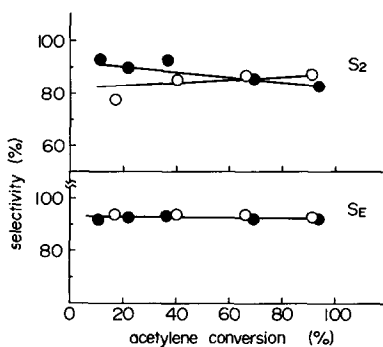

FIG. 1. Hydrogenation of acetylene on sulfurated nickel at 119°C. Initial pressure are $C_2H_2 = 19.8$ mm Hg and $H_2 = 39.0$ mm Hg.

FIG. 2. Dependence of selectivities upon acetylene conversion on nickel (○) and sulfurated nickel (●).

activity is increased by these treatments as well as by repeated uses of the catalyst. In this series of experiments, none of sulfur compounds were detected in gas phase with mass spectrometer. These facts suggest that nickel is enriched on catalyst surface by diffusion of sulfur into metal bulk and this was proved by AES analysis.

Hydrogenation of ethylene on freshly sulfurated nickel was so slow as to give only 2% of conversion in 45 hr at 120°C, while consecutive hydrogenation of produced ethylene is obviously accelerated in a brief time after the exhaustion of acetylene as shown in Fig. 1 and more clearly in Fig. 3.

These results and the presence of induction period infer that the freshly sulfurated surface (surface I) is changed during the induction period to surface II being active for hydrogenation of acetylene as well as ethylene, and that the surface II goes back reversibly to surface I by exhaustion of acetylene.

Experiments given in Fig. 4 ensures this inference. The addition of acetylene during its hydrogenation gave no activity change, whereas obvious induction phenomena were observed after several hours of complete consumption of acetylene or by trapping of acetylene with liquid nitrogen.
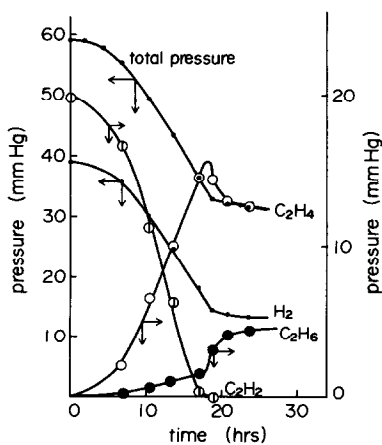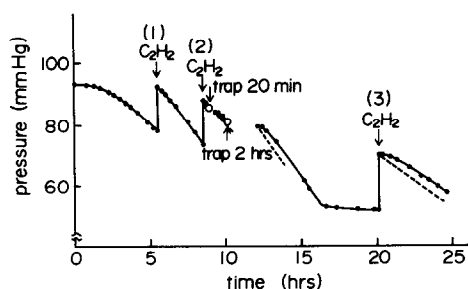

FIG. 4. Induction phenomena during acetylene hydrogenation on sulfurated nickel at 119°C. Initial pressures are $C_2H_2 = 18.9$ mm Hg and $H_2 = 74.3$ mm Hg. Arrows (1), (2) and (3) the addition of acetylene; (○) removing of acetylene by trapping; (---) slopes expected at no induction period.

The surface I of sulfurated nickel is also inactive for the H_2–D_2 equilibration reaction except the abnormal isotopic mixing at the initial few minutes. When acetylene is added to a mixture of H_2 and D_2, hydrogenation starts with an induction period. If acetylene is removed from the reacting gas with liquid nitrogen trap, then H_2–D_2 equilibration reaction proceeds markedly for a brief time, as shown in Fig. 5, similarly to the consecutive hydrogenation of ethylene demonstrated in Fig. 3. The surface II, but not the surface I, of sulfurated nickel is thus proved to be active for the H_2–D_2 equilibration as well as hydrogenation.

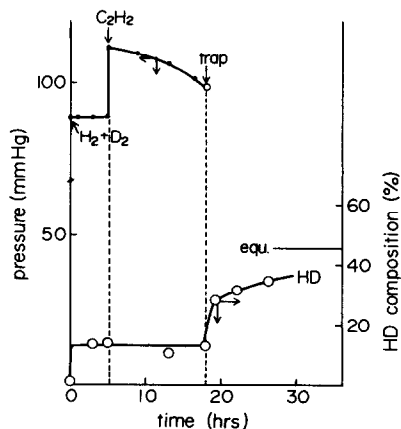FIG. 3. Hydrogenation of acetylene on sulfurated nickel at 119°C (run 2 of Fig. 1).

FIG. 5. Equilibration reaction of H_2 and D_2 ($H_2/D_2 = 2/3$) on sulfurated nickel at 120°C. Acetylene is added at 5.1 hr and trapped at 18.0 hr. (equ.) An equilibrium composition.

Deuterium distribution in acetylene, eth-
ylene and ethane formed by the reaction of
acetylene with a mixture of H_2 and D_2
($H_2/D_2 = 2/3$) is given in Table 2. Eth-
ylene-d_0, -d_1 and -d_2 are the main species
of deuteroethylene, obviously differing
from a random distribution of D atoms.
Even though the measurement is less accu-
rate, relative abundances of deu-
teroethanes from -d_1 to -d_6 are given in
Table 2. Deuterium is not found in acety-
lene at all, revealing that acetylene adsorbs
irreversibly on sulfurated nickel.

Hydrogenation of acetylene on nickel
sulfides was studied out to compare with
sulfurated nickel. On nickel sulfide of
S/Ni = 0.02, acetylene was hydrogenated
to ethane without induction period as was
the case of nickel catalyst (9,12,13). In
contrast with this, the selective partial hy-
drogenation of acetylene to ethylene and a
marked induction period were observed on

the nickel sulfide of S/Ni = 0.62. Thus the
partial hydrogenation of acetylene closely
relates to the presence of an induction
period. The composition of the reaction
products over the sulfide of S/Ni = 0.62
was similar to those over the nickel (9) and
the sulfurated nickel. Hydrogenation of
acetylene over this sulfide was reprodu-
cible in contrast with the sulfurated nickel
(S/Ni = 10^{-4}), suggesting that a steady
ratio of nickel to sulfur on the sulfide
makes a reproducible activity in contrast
with the rising of activity on sulfurated
nickel. On the other hand, the nickel sul-
fide having ratio of S/Ni = 0.96 was inac-
tive for hydrogenation of acetylene, re-
vealing that nickel atoms of this sulfide are
coordinatively saturated by sulfur.

Figure 6 shows a typical result of AES
measurement of freshly sulfurated nickel,
and the changes of the peak–peak ampli-
tude are plotted as a function of sputtered
depth L. Sulfur diffuses in nickel bulk as
deep as 500 Å, showing that sulfur is con-
siderably mobile in nickel bulk. Peak–peak
amplitude of 152 eV sulfur peak decreases
at the surface as shown in Fig. 6, which
may be masked by the adsorbed of oxygen
and impurities came from air.

Figure 7 shows the result of AES analy-
sis of a NiS disk. Each peak–peak ampli-
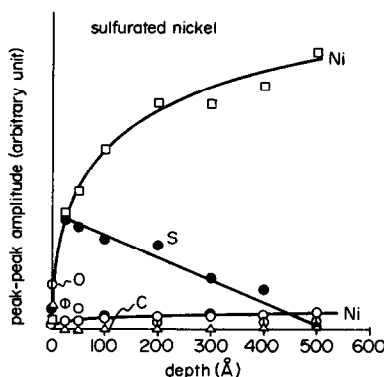tude is constant in bulk phase, suggesting

TABLE 2

DEUTERIUM DISTRIBUTIONS (%) IN ACETYLENE,
ETHYLENE AND ETHANE FORMED BY C_2H_2
HYDROGENATION WITH H_2–D_2 MIXTURE
IN FIG. 5

Time (hr):	12.9	17.9
Ethylene-d_4	4.3	3.6 (0.6)[a]
d_3	5.7	6.4 (6.3)
d_2	19.0	20.4 (24.4)
d_1	35.0	36.6 (41.8)
d_0	36.0	33.0 (26.9)
Av D content (%)	27	28
Ethane-d_6	—	0.8 (0.2)
d_5	—	2.8 (2.3)
d_4	9.9	9.2 (10.1)
d_3	21.1	19.3 (24.3)
d_2	43.2	33.9 (32.7)
d_1	25.8	34.0 (23.4)
d_0	—	— (7.0)
Av. D content (%)	36	36
Acetylene-d_1, -d_2	0	0
d_0	100	100

[a] Parentheses show the random distribution of
deuterium.

FIG. 6. AES analysis of sulfurated nickel having
been contacted with ethylene; Ni at 61 eV (□), Ni at
783 eV (○), S at 152 eV (●), C at 272 eV (△) and O
at 510 eV (⊕).
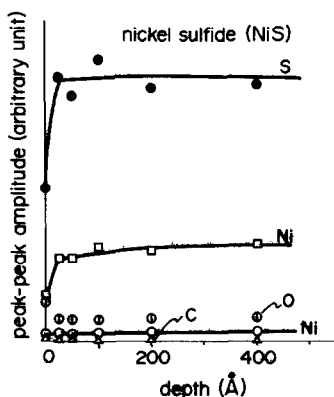
FIG. 7. AES analysis of standard NiS sample. Assignment of plots is the same as Fig. 6.

A nickel catalyst poisoned by a trace of CO also enhances the partial hydrogenation of acetylene and 1,3-butadiene (7).

Nickel atom in Ni_3S_2 is surrounded by four S atoms, while by six S atoms in NiS, and hence Ni atoms on the surface of Ni_3S_2 as well as sulfurated nickel may have appropriate coordinative unsaturation of nickel atoms in contrast with NiS. In conclusion, the partial hydrogenation is mainly controlled by reversible formation of coordinatively unsaturated nickel atoms being generated by replacing with acetylene.

that the change of bulk composition caused by the argon ion bombardment, if any, is negligible. Peak–peak amplitude of nickel at 61 eV changes in parallel with that of sulfur at 152 eV. On account of escape depth of electron (14), nickel peak at 61 eV is more appropriate than that at 783 eV to estimate the ratio S/Ni on the catalyst surface. Figure 7 shows that peak of sulfur is three times as sensitive as that of nickel at 61 eV. Figure 8 is obtained from Fig. 6 by the use of above ratio of sensitivity of sulfur to nickel. Atomic ratio S/Ni of the sulfurated nickel surface is estimated as 0.69 which is nearly equal to 0.67 of nickel subsulfide Ni_3S_2 known as an effective catalyst for selective partial hydrogenation (6).
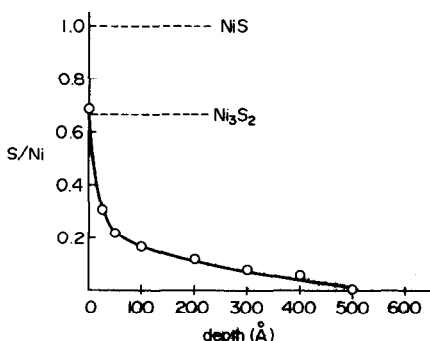
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FIG. 8. Change of atomic ratio S/Ni in sulfurated nickel along the sputtered depth. (--) Values for stoichiometric NiS and Ni_3S_2.

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