

REVERSIBLE FORMATION OF ACTIVE SITES  
ON SULFURATED NICKEL CATALYST

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The active sites for hydrogenation are formed on sulfurated nickel by displacing sulfur atoms with acetylene, and when acetylene is exhausted, the sites are occupied by sulfur to result in inactive. The above process is ensured with the  $H_2$ - $D_2$  equilibration reaction, and makes clear the characteristic of the partial hydrogenation of acetylene over sulfurated nickel.

The high selectivity of partial hydrogenation of acetylene was observed by Kwan et al. over sulfurated nickel<sup>1)</sup> but the details of the reaction was not studied in their work.

This paper makes clear the characteristics of the sulfurated nickel catalyst in the hydrogenations of ethylene and acetylene.

The reaction was carried out in a conventional closed circulation system of about 600 ml. Nickel wire ( 0.1 mm diameter and 210 m length ) was mounted in a reactor and was treated with 1.0 mmHg  $H_2S$  at 300°C for 2 minutes. The estimated amount of sulfur deposited was more than monolayer<sup>5)</sup> and might form a layer of surface compound such as  $Ni_3S_2$ .<sup>7)</sup>

The activity is very low at the initial stage of the reaction especially on a freshly prepared sulfurated nickel. The induction phenomenon is observed and the consecutive hydrogenation of produced ethylene is very slow as shown by solid curves in Fig. 1(a). The induction phenomenon and the slow consecutive hydrogenation of ethylene are the characteristics of the sulfurated nickel in contrast with the reaction on nickel catalyst.<sup>2)3)6)</sup>

The hydrogenation of ethylene at 120°C on freshly prepared sulfurated nickel gave only 2% of conversion after 45 hours, indicating the sulfurated nickel is inactive for the hydrogenation of ethylene in contrast with the hydrogenation over the sulfurated tungsten.<sup>4)</sup> A similarity is observed in the hydrogenations of butenes and 1,3-butadiene, that is, the hydrogenation of butenes is hard to proceed on the sulfurated nickel but the hydrogenation of 1,3-butadiene takes place on it as shown in Fig. 1(b).

After the first run, (1), the sulfurated nickel was reduced with hydrogen at 300°C and the next reaction, (2), was carried out on it. The catalytic activity is clearly increased by the reduction with hydrogen as shown in Fig. 1(a) but  $H_2S$  could not be detected by a mass-spectrometer in the hydrogen gas used for reduction.

The run (3), carried out on the catalyst which had been left for a long time more than a week in contact with the reacted gas of run (2) and then evacuated at

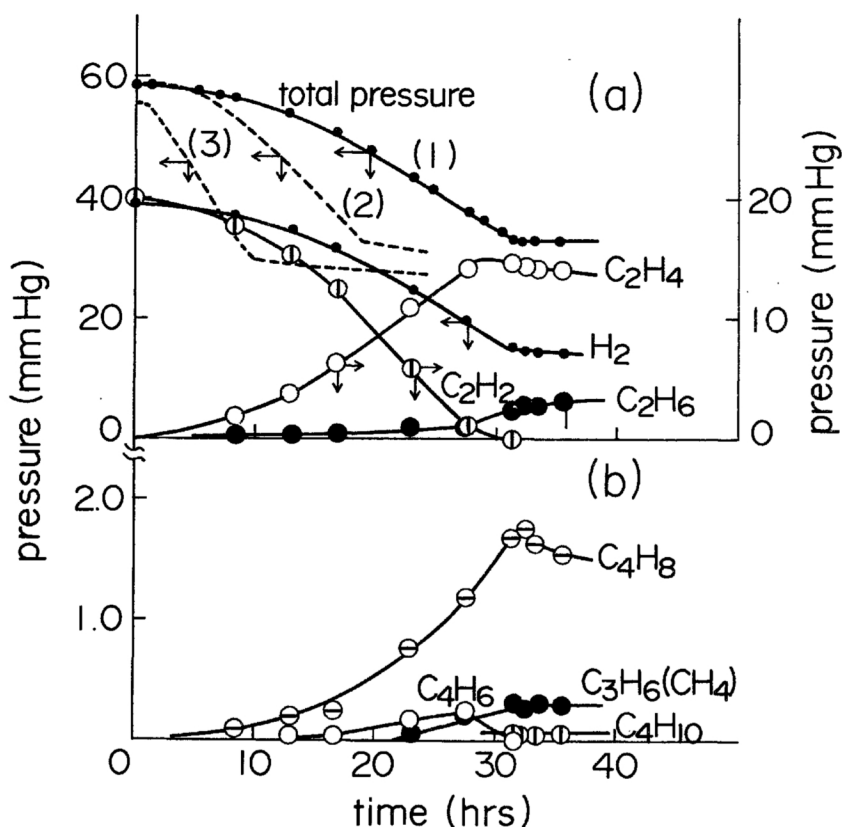


Fig. 1 Hydrogenation of acetylene on sulfurated nickel at 119°C. The initial pressures;  $P_{C_2H_2} = 19.8$  mmHg,  $P_{H_2} = 39.0$  mmHg.

119°C but not been reduced at 300°C, gave the higher activity than the run (2). The activity was increased by repeating the same procedure and the induction period became shorter, however none of sulfur compounds such as  $H_2S$  or thiophene were detected in reacting gas as ascertained by the absence of the peaks of  $H_2S^+$  and  $HS^+$  in mass-spectra.

These facts may suggest that the sulfur coated on the surface diffuses into the metal bulk.

Merely ethylene and ethane in the run (2) are shown in Fig. 2. Consecutive hydrogenation of produced ethylene is obviously accelerated at the complete consumption of acetylene but slows down quickly. This may indicate that the surface active for the hydrogenation of acetylene is also active for the hydrogenation of ethylene but loses the activity quickly in the absence of acetylene.

If the induction phenomenon observed at the initial stage of the reaction is the formation process of the active sites by displacing the sulfur atoms with adsorbed acetylene, the active sites for the hydrogenation may be reoccupied by the sulfur atoms when acetylene is exhausted and results in inactive for the hydrogenation of produced ethylene.

In order to ensure this inference, several experiments showing relations bet-

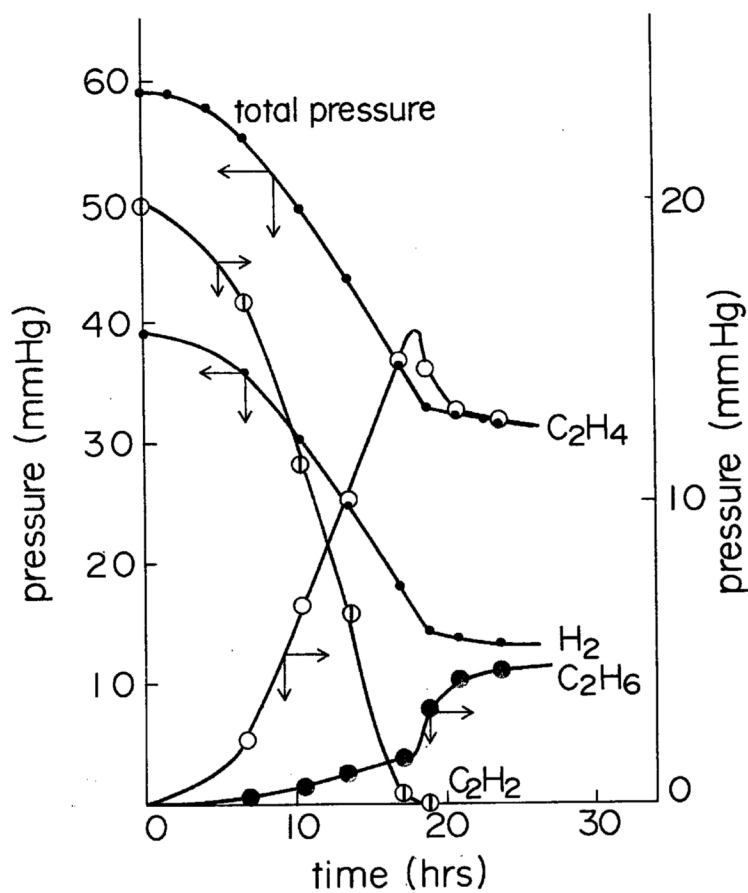


Fig. 2 Hydrogenation of acetylene on sulfurated nickel at 119°C (run (2) in Fig. 1).  
The initial pressures;  $P_{C_2H_2} = 19.9$  mmHg,  
 $P_{H_2} = 39.2$  mmHg.

ween the induction phenomenon and the activity were carried out. The addition of acetylene during the reaction gives no induction phenomenon but the addition of acetylene after the several hours of complete consumption or trapping of acetylene with liquid nitrogen gives induction phenomena as shown in Fig. 3. The longer trapping interval resulted in the longer induction period.

These results support the inference that sulfur is displaceable from the active sites reversibly with acetylene adsorbed competitively. This model of the active sites is also supported by the  $H_2$ - $D_2$  equilibration reaction during the hydrogenation reaction.

Sulfurated nickel is inactive for the  $H_2$ - $D_2$  exchange reaction except the initial few minutes after the introduction of the mixture of  $H_2$  and  $D_2$ . However, if acetylene was trapped during the hydrogenation of acetylene with the mixture of  $H_2$  and  $D_2$ , the  $H_2$ - $D_2$  exchange reaction is clearly accelerated as shown in Fig. 4. The exchange

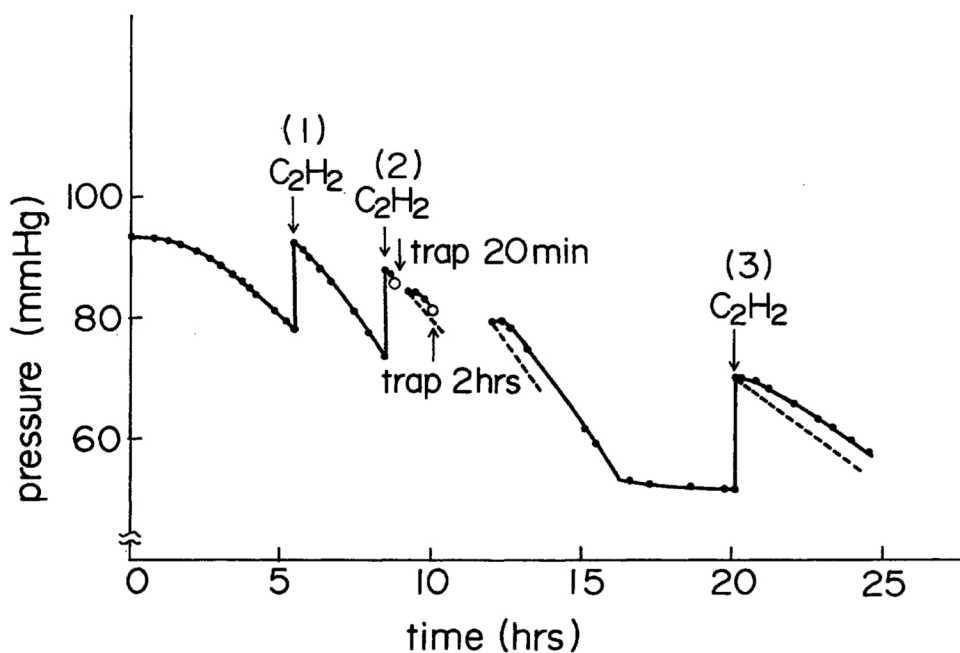


Fig. 3 Induction phenomena during the acetylene hydrogenation at 119°C. The initial pressures;  $P_{C_2H_2} = 18.9$  mmHg,  $P_{H_2} = 74.3$  mmHg. Arrows at (1), (2) and (3); the addition of acetylene. Open circles; trapping of acetylene. Dotted lines; the expected slopes for the none induction.

reaction, however, slows down quickly as observed in the consecutive hydrogenation of ethylene shown in Fig. 2.

Accordingly, the characteristic of partial hydrogenation of acetylene on sulfurated nickel is originated from the co-ordination strength of sulfur, acetylene and ethylene to nickel atoms in the order of  $C_2H_2 > S > C_2H_4$ .

The similarity has been found in the poisoning of nickel by carbon monoxide. By adding a small amount of carbon monoxide on the way of reaction, the hydrogenations of acetylene and 1,3-butadiene take few effects but the hydrogenation of mono-olefines are retarded distinctly as shown in Fig. 5.

The hydrogenation of ethylene did not proceed over carbon monoxide preadsorbed nickel, but produced ethylene is hydrogenated consecutively on this catalyst after the hydrogenation of acetylene. This indicates that carbon monoxide adsorbed on nickel may be kicked out into gas phase by the adsorption of acetylene in contrast with the case of sulfur remaining on the surface.

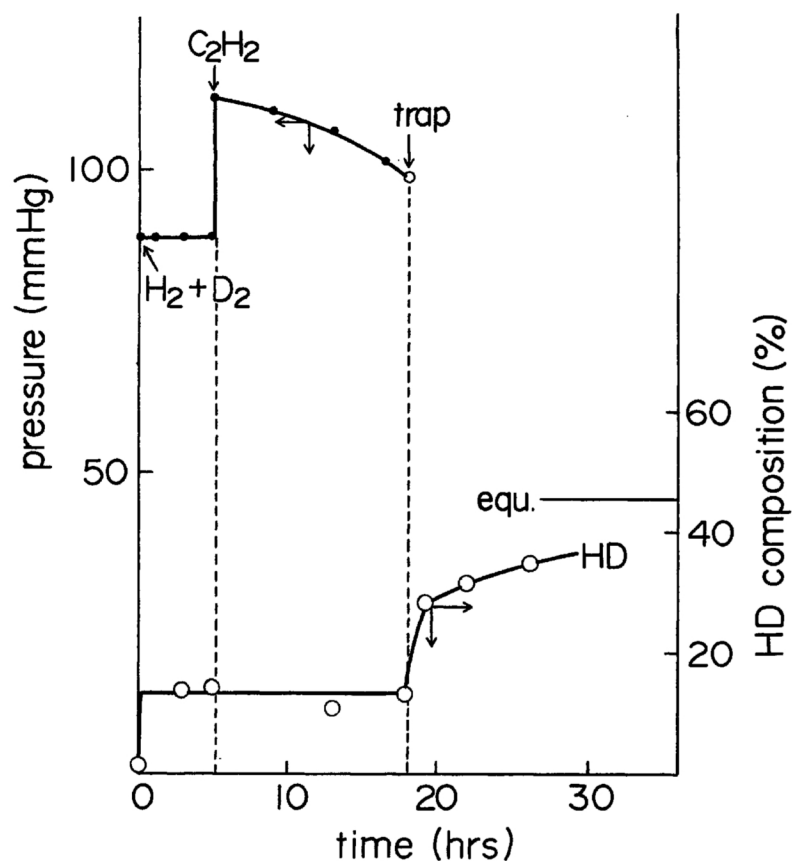


Fig. 4 The  $\text{H}_2$ - $\text{D}_2$  exchange reaction on sulfurated nickel at  $120^\circ\text{C}$ . The initial ratio of  $\text{H}_2$  to  $\text{D}_2$  was  $2/3$  and the equ. indicates the calculated equilibrium composition. Acetylene is added at 5.1 hrs and is trapped at 18.0 hrs.

Consequently co-ordination strength to nickel atoms is described in the order  $\text{C}_2\text{H}_2, \text{C}_4\text{H}_6 > \text{S}, \text{CO} > \text{C}_2\text{H}_4, \text{C}_4\text{H}_8$ , which makes the characteristic partial hydrogenation of acetylene possible.

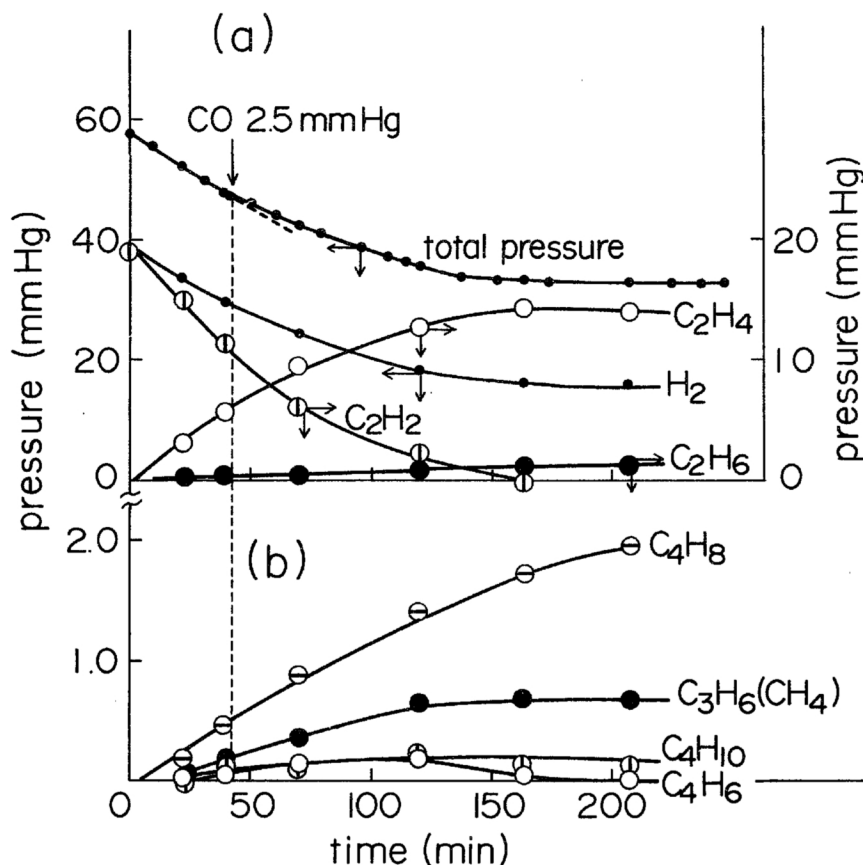


Fig. 5 The effect of added CO on the hydrogenation reactions at 151°C. The initial pressures;  $P_{C_2H_2} = 19.2$  mmHg,  $P_{H_2} = 38.3$  mmHg.

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