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CATALYSIS AND COORDINATIVE UNSATURATION OF THE SULFURATED NICKEL SURFACE

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Sulfurated nickel is catalytically inactive for the hydrogenation of olefin but active for the isomerization of butene and the C_2H_4-C_2D_4 exchange reaction in coexistence of hydrogen.

On contaction with acetylene, the surface becomes active for the hydrogenation of olefin and the H_2-D_2 equilibration as well as the hydrogenation of acetylene. These characteristics are well described by the degree of coordinative unsaturation of active sites suggested by Siegel.

The authors have found that the catalytic activity and/or the selectivity of sulfurated nickel for the partial hydrogenation of acetylene is controlled by displacement of sulfur atoms on active sites with acetylene.1) In the homogeneous catalysis by metal complexes, the activity and/or the selectivity of the catalyst have been discussed on the basis of the configuration of the catalyst and its degree of coordinative unsaturation (the number of vacant sites available for coordination), while in the heterogeneous catalysis these have been mainly explained by the competitive adsorption of reacting species and/or the relative rates of each reaction.2)

This communication gives some evidence suggesting that the catalytic activity and/or the selectivity of sulfurated nickel is mainly controlled by the degree of coordinative unsaturation of active sites.

The reactions were carried out in a conventional closed circulation system used in the previous work. A nickel wire of 130 m in length and 0.1 mm in diameter was treated with 0.8 mmHg H_2S at 300°C for 2 minutes and was evacuated for 4 minutes at 300°C. The estimated amount of sulfur deposited was more than monolayer.1)

When 1-butene alone was admitted to sulfurated nickel, neither the self-hydrogenation nor the isomerization of butene were observed in 5.8 hrs at 120°C.

On the other hand, if a mixture of 1-butene and hydrogen was admitted at 121°C, the isomerization of butene having no induction period was observed, but the hydrogenation of butene to n-butane is only 1.7% in 6.1 hrs as shown in Fig. 1. The gas phase was then evacuated for 2 minutes at 121°C and a mixture of acetylene and hydrogen was introduced. Obvious induction period was observed for acetylene hydrogenation as shown in Fig. 1, indicating that the surface during the butene isomerization is inactive for the hydrogenation of acetylene as well as olefin. 1)

In order to elucidate the role of hydrogen, the isomerization of 1-butene was

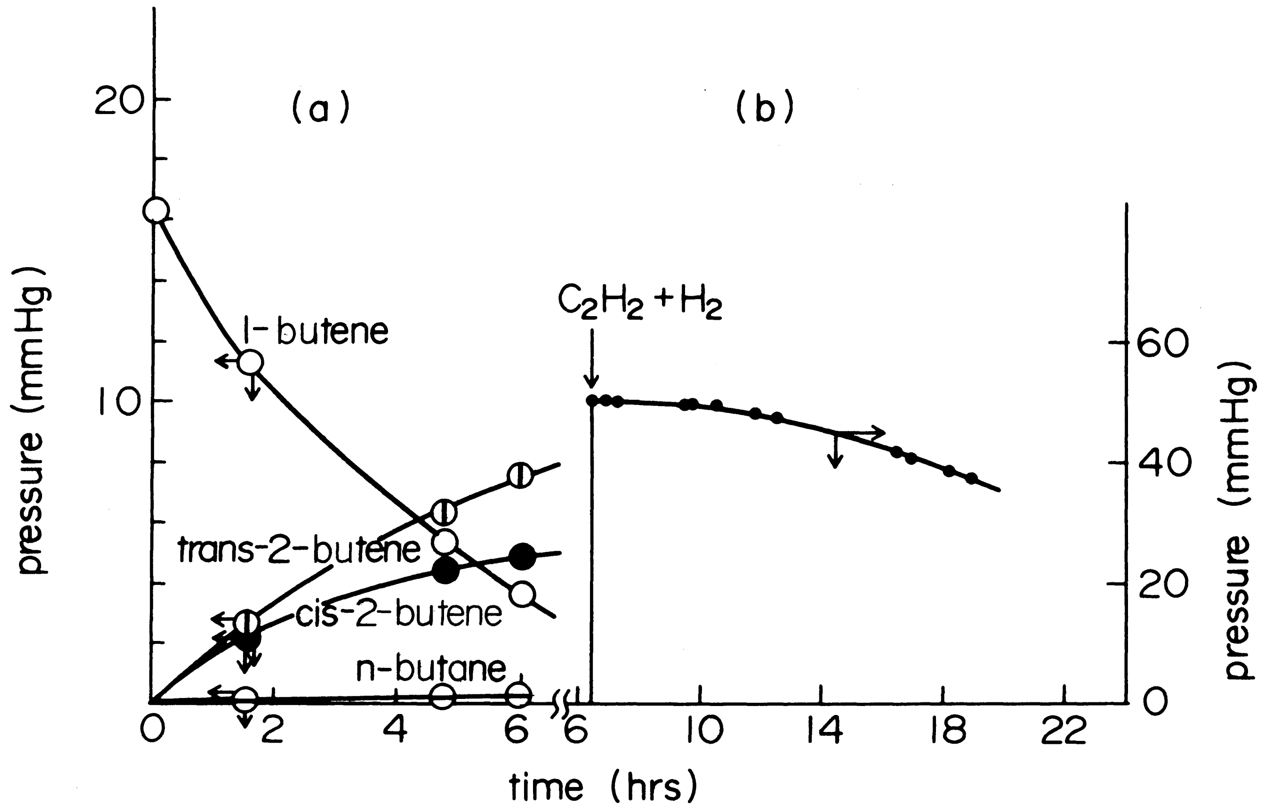


Fig. 1 (a): isomerization of 1-butene over sulfurated nickel at 121°C in coexistence of hydrogen, the initial pressures are 1-butene=16.3 mmHg and H_2=32.9 mmHg.
(b): hydrogenation of acetylene at 121°C on the catalyst having been used for the isomerization, the initial pressures are C_2H_2=17.0 mmHg and H_2=33.2 mmHg.

carried out on freshly sulfurated nickel in the presence of deuterium at 121°C. The initial pressures of 1-butene and deuterium (containing 1.2% of HD) were 19.7 mmHg and 37.9 mmHg, respectively.

The analysis of deutero-butenes (d_j) was made without separating into the isomers by a mass spectrometer at 12.5V of the ionization voltage. The results presented in Table 1 show that the isotopic mixing between hydrogen and butene is entirely slow as compared with the isomerization.

A similar phenomenon was observed on the exchange reaction between C_2H_4 and C_2D_4 on freshly sulfurated nickel. The exchange reaction was obviously accelerated by the addition of hydrogen gas as shown in Fig. 2, whereas the isotopic mixing between hydrogen and ethylene is negligible as shown in Table. 2.

On the basis of these results the isomerization of butene and the C_2H_4-C_2D_4 exchange reaction are concluded to proceed via the half-hydrogenated butyl and ethyl intermediates respectively, where the hydrogen irreversibly supplied from gas phase

Table 1. Isomerization of 1-butene and the isotopic mixing in butene and in hydrogen

time (hrs)	1.4	3.1	5.7	7.4	equilibrium
1-butene	75.6%	60.8	44.5	36.8	(7.7%)
trans-2-butene	13.4	21.9	32.8	38.4	(63.9)
cis-2-butene	11.0	17.3	22.7	24.8	(28.4)
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	
$\geq d_3$	0	0	0	0	
average 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	

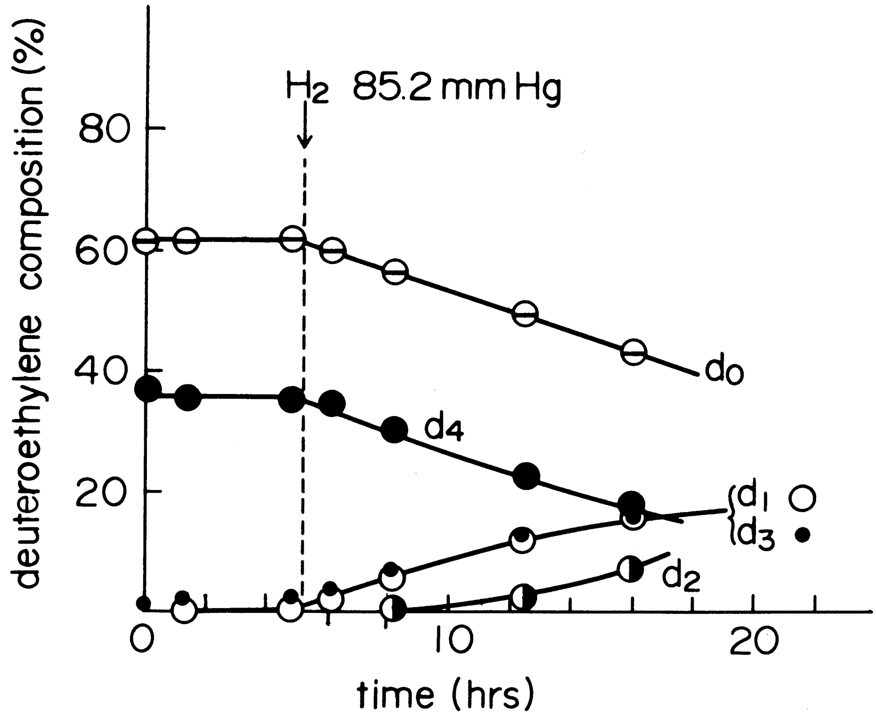


Fig. 2. The effect of addition of hydrogen on the exchange reaction between C_2H_4 (d_0) and C_2D_4 (d_4) over sulfurated nickel at 121°C. Initial composition of an ethylene mixture was d_0=61.5%, d_3=1.7% and d_4=36.8% at a total pressure of 41.1 mmHg. Hydrogen was added at 5.2 hrs indicated with a broken line.

Table 2. The change of isotope composition of hydrogen during the C_2H_4-C_2D_4 exchange

time (hrs)	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

acts as a kind of co-catalyst over sulfurated nickel.

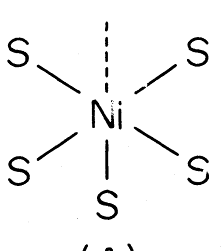
The characteristics of catalyses over sulfurated nickel are summerized in Table 3, where surface (I) is freshly sulfurated nickel surface being inactive for all the types of reactions. Surface (I-H_2) is surface (I) modified with hydrogen being active for the isomerization of butene and the C_2H_4-C_2D_4 exchange reaction. Surface (II) is formed by contacting with acetylene and is active for the hydrogenation of olefin and the H_2-D_2 equilibration reaction as well as the acetylene hydrogenation.$^{1)}$

Table 3. The classification of active sites (+; active and -; inactive)

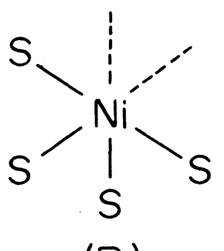
	surface		
reactions	(I)	(I-H_2)	(II)
isomerization of butene	-	+	(+)
exchange of C_2H_4-C_2D_4	-	+	(+)
hydrogenation of C_2H_2		-	+
hydrogenation of C_2H_4 or C_4H_8		-	+
exchange of H_2-D_2		-	+
exchange of H_2-C_2D_4, D_2-C_4H_8		-	

Siegel has recently proposed a model showing the configuration of active sites on solid surface and the reactions may take place over it.$^{3)}$

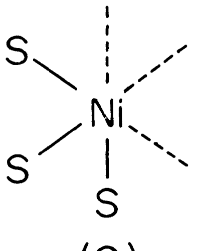
Surface (I) in the present case corresponds to type (A) and/or type (B) sites in Siegel's model, and surface (II) corresponds to type (C) sites. The degree of coordinative unsaturation of type (A), type (B) and type (C) sites are one, two and three fold respectively.



(A)

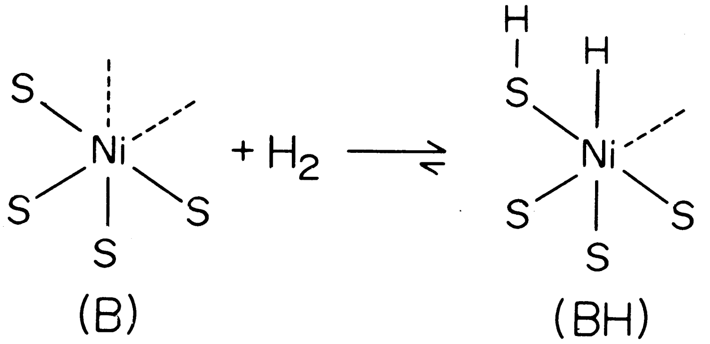


(B)

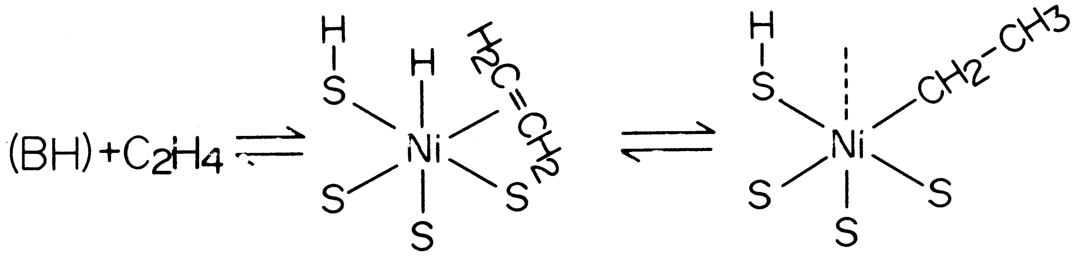


(C)

When surface (I) is contacted with hydrogen, surface (I-H_2), type (BH) sites are formed by equation (1), on which the C_2H_4-C_2D_4 exchange reaction and the isomerization of butene may take place according to forward and backward processes of equation (2).



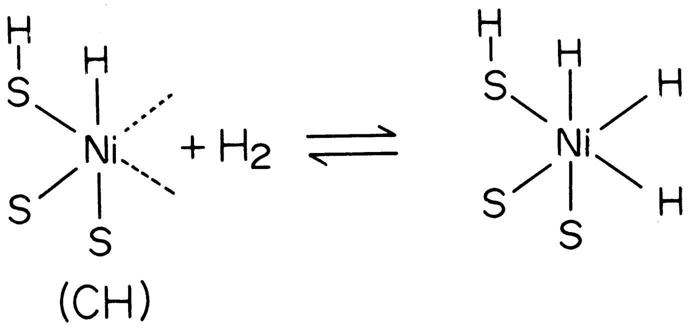
(1)



(2)

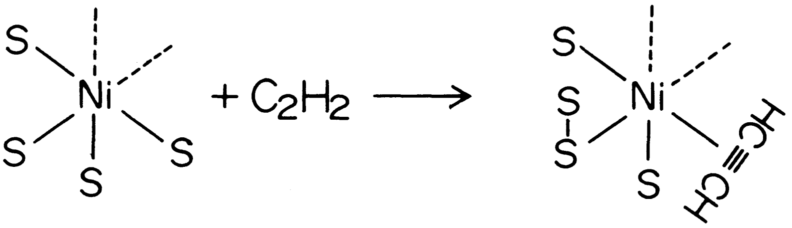
The reverse process of equation (1) should be very slow[3)] because the isotopic mixing between hydrogen and olefins during the isomerization of butene and the C_2H_4-C_2D_4 exchange reaction is entirely slow. Accordingly the hydrogen atom on nickel acts catalytically to promote the reactions without consumption of hydrogen.

We may easily understand that the hydrogenation of olefin and acetylene is difficult to proceed on types (A) and (B) sites, but able on type (C) sites, e.g. surface (II), having three fold coordinative unsaturation because both hydrogen and olefin or acetylene are able to coordinate on a nickel at the same time.[3)] The H_2-D_2 equilibration reaction is also hard to proceed on types (A) and (B) or (BH) sites, e.g. surface (I) or (I-H_2), but is possible on type (CH) sites, hydrogenated (C), according to equation (3).



(3)

The results obtained in the present work lead us to a conclusion that the freshly sulufurated nickel surface is constructed by type (A) and/or type (B) sites, and type (C) sites are formed by displacing sulfur atoms with acetylene$^{1)}$ according to equation (4), on which the hydrogenation and the H_2-D_2 exchange reaction can take place.$^{1)}$



(B) (C) (4)

When acetylene is consumed, type (C) sites are reoccupied by sulfur to become type (B) sites again and result in inactive for the hydrogenation reactions. This reversible change of the degree of coordinative unsaturation of active sites controls strictly the selective hydrogenation of acetylene to ethylene on sulfurated nickel. The sequence of coordinative strength to nickel ($C_2H_2 > S > C_2H_4$) mentioned in the previous work$^{1)}$ represents the ability for the formation of type (C) sites.

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