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Hydrogenation of 1,3-Butadiene by Cyclohexadiene over CoS Catalyst

KATSUMI TANAKA, KEN-ICHI TANAKA AND KOSHIRO MIYAHARA

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

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Selective formation of butenes from 1,3-butadiene was performed by the reaction with cyclohexadiene (CHD) over CoS, which was inactive for 1,3-butadiene hydrogenation with molecular hydrogen. Isomeric composition of formed butene was the same with 1,3- and 1,4-CHD. The catalyst catalyzed the disproportionation of CHD to benzene, cyclohexene, and hydrogen as well as butadiene hydrogenation, indicating the competitive hydrogen transfer from CHD to butadiene and CHD. The hydrogen transfer, we concluded, took place not through direct hydrogen transfer between these molecules but through hydrogen atoms once released from CHD onto the catalyst surface.

INTRODUCTION

Catalyzed hydrogenation of olefins and other unsaturated substances has been carried out (*1–4*) using hydrogen compounds as a hydrogen source. Most of the catalysts used in these experiments were Pd, and others were catalytically active for hydrogen chemisorption as well as for hydrogenation with molecular hydrogen. Compounds of hydrogen donor were considered to be a source of chemisorbed hydrogen atoms similar to hydrogen gas. However, there are some exceptions to this point of view; for instance, MgO heated in advance at ca. 1000°C in a vacuum showed a high catalytic activity for 1,3-butadiene hydrogenation with molecular hydrogen even at 0°C (*5*), in spite of its practical inactivity for H_2–D_2 equilibration, and RhCl (CO) $(PPh_3)_2$ complex which was inactive for olefin hydrogenation with molecular hydrogenation, was still active for hydrogenation of 1-octene with formic acid (*6*).

We have found, on the other hand, in the study of the catalytic behavior of several metal sulfides (*7*) that cobalt sulfides CoS_2 and CoS, hardly catalyzed the hydrogenation of 1,3-butadiene by hydrogen gas, even though they were heated in advance *in vacuo* at 450°C for several hours and the reaction temperature was raised up to 240°C (*8*).

The catalytic behavior of CoS for 1,3-butadiene hydrogenation by cyclohexadiene (CHD) was investigated in the present work, and it was clearly illustrated that a solid inactive for hydrogen chemisorption is still active for hydrogenation of adsorbable olefin when atomic hydrogen is supplied by a process other than hydrogen chemisorption.

EXPERIMENTAL

Five grams of CoS (99.9% purity) was used for every run of reaction after evacuation at 450°C for 3 hr. The reaction was carried out at 240°C in the usual circulation system equipped with greaseless valves.

Hydrocarbons were purified by distillation repeated *in vacuo* between traps cooled at 78 and 193 K. Hydrogen gas was purified

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by passing it through a Pd–Ag thimble and then through a trap with 5A molecular sieves which were cooled to 78 K just before the reaction.

Products of reaction were analyzed with a gas chromatograph equipped with a VZ-7 column (4 mm × 6 m) at 0°C for C_4-hydrocarbons and with a PEG-200 column (4 mm × 2 m) at 0°C for C_6-hydrocarbons; sampled gas was allowed to flow into these columns alternately with H_2 carrier. Deuterium distribution in butene and butadiene was estimated mass spectrometrically from the relative heights of the parent peaks obtained with an ionization voltage of 12 to 14 V. For deuterated hydrogen gas the ionization voltage was fixed at 70 V, and its isotopic composition was estimated with reference to a spectrum of equilibrated hydrogen of known deuterium fraction.

RESULTS

Figures 1 and 2 show the results obtained over CoS catalyst at 240°C with a 1:2 mixture of 1,3-butadiene and 1,3- or 1,4-CHD. They illustrate the remarkable catalytic activity of CoS for disproportionation and isomerization of CHD as well as butadiene hydrogenation. These reactions did not take place without the catalyst.

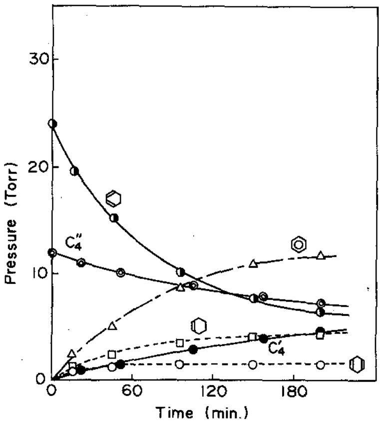


FIG. 1. Reaction of butadiene (C_4'') with 1,3-cyclohexadiene over CoS at 240°C. (1 Torr = 133.3 N/m²).

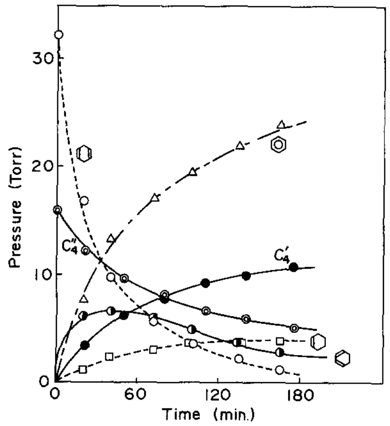


FIG. 2. Reaction of butadiene with 1,4-cyclohexadiene over CoS at 240°C.

The kinetic behavior of the reaction between 1,3-butadiene and CHD was examined at 240°C by abruptly increasing butadiene or CHD partial pressure from P_1 to P_2 in the course of the reaction. The results are given in Fig. 3 where v_1 and v_2 are the initial formation rates of a given product at P_1 and P_2, respectively. We see that the formation rate of every butene isomer is first order and zero order with respect to CHD and butadiene, respec-

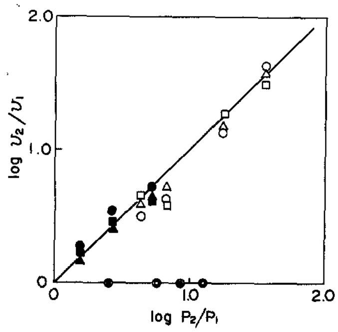


FIG. 3. Course kinetics of the reaction of butadiene with 1,3- or 1,4-cyclohexadiene over CoS at 240°C. v_1 and v_2 are the formation rates of the respective product at P_1 and P_2 of 1,3- or 1,4-cyclohexadiene (CHD). (○) 1-Butene, (△) *trans*-2-butene, (□) *cis*-2-butene in the reaction with 1,4-CHD; (●) 1-butene, (▲): *trans*-2-butene, (■) *cis*-2-butene in the reaction with 1,3-CHD.

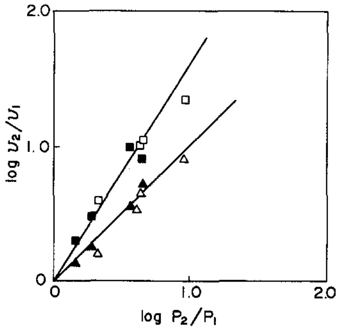


Fig. 4. Course kinetics of cyclohexadiene disproportionation over CoS at 240°C. (□, ■) Cyclohexene, and (△, ▲) benzene formed from 1,4-CHD (open symbols) and 1,3-CHD (closed symbols), respectively.

tively, while the disproportionation rates of CHD at different CHD partial pressures differed for the formation of benzene and cyclohexene, as shown in Fig. 4. However, the initial rates of formation of benzene and cyclohexene at 200°C were commonly zero order with respect to the initial partial pressure of CHD. We concluded that this discrepancy in the kinetics of disproportionation was caused by the effect of one of the products, benzene, which will be discussed later.

The product distribution of butadiene hydrogenation with CHD at 240°C was the same for 1,3- and 1,4-CHD as shown in Fig. 5; the ratio of 2-butene/1-butene at an early stage was far smaller than that at equilibrium (~7), while the ratio of *cis*-2-butene/*trans*-2-butene was close to the equilibrium value (~0.6).

The slow H_2–D_2 equilibration over CoS at 240°C was almost unaffected by the predominant evolution of hydrogen from CHD as shown in Fig. 6. Deuterium distributions in the products of butadiene hydrogenation with a mixture of CHD and D_2 are given in Table 1, where we see that the majority of butadiene and butene was

TABLE 1

Deuterium Distributions in Butene and Butadiene Formed by Reaction of Butadiene, Cyclohexadiene, and D_2 over CoS at 240°C

Time (min)	Hydrocarbon	Composition (%)	Deutero isomer (%)			
			d_0	d_1	d_2	d_3
	A. Butadiene + 1,4-cyclohexadiene + D_2(1:1:1)					
10	1-Butene	3.6	92.9	6.4	0.7	0
	trans-2-Butene	2.6	94.1	5.5	0.4	0
	cis-2-Butene	1.1	95.0	4.8	0.2	0
	Butadiene	92.6	99.5	0.5	0	0
60	1-Butene	13.1	90.4	8.8	0.8	0
	trans-2-Butene	10.1	91.1	7.6	1.3	0
	cis-2-Butene	5.3	91.5	7.6	0.9	0
	Butadiene	71.6	96.9	2.4	0.7	0
	B. Butadiene + 1,3-cyclohexadiene + D_2(1:1:1)					
30	1-Butene	3.1	90.4	8.5	1.1	0
	trans-2-Butene	2.6	91.2	7.6	1.2	0
	cis-2-Butene	1.7	93.0	6.1	0.9	0
	Butadiene	92.6	99.8	0.2	0	0
180	1-Butene	12.9	86.0	12.4	1.4	0.2
	trans-2-Butene	11.1	86.7	11.5	1.5	0.3
	cis-2-Butene	6.1	87.1	11.3	1.3	0.2
	Butadiene	69.9	95.1	4.1	0.8	0

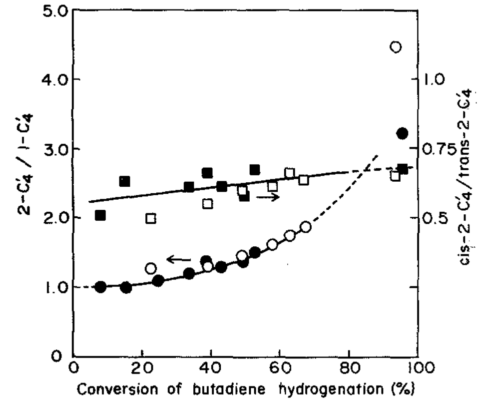


FIG. 5. Relative amounts of butene isomers formed by the reaction of butadiene with CHD over CoS at 240°C. Open or closed symbols represent the reaction with 1,4- or 1,3-CHD, respectively.

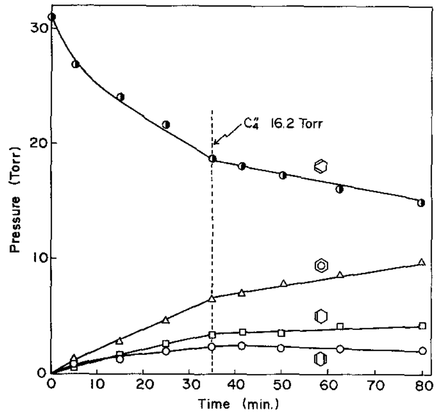


FIG. 7. Effect of butadiene addition on the reaction of 1,3-CHD over CoS at 240°C.

not deuterated; that is, hydrogen exchange between CHD and D_2, if any, was slow and butadiene was hydrogenated solely by hydrogen from CHD. Table 1 shows, furthermore, that butane was absent; that is, the partial hydrogenation of butadiene was perfect using CHD.

Figure 7 shows the effect of butadiene on the hydrogenation of 1,3-CHD into cyclohexene, the dehydrogenation into benzene, and the isomerization into 1,4-CHD, where the addition of butadiene retards both the hydrogenation and the isomerization reaction. It is worthwhile to mention that benzene formation undergoes less retardation than is expected from the effect on cyclohexene formation; that is, less of the hydrogen atoms generated from 1,3-CHD can be used in cyclohexene formation. The reaction was neither affected by the addition of butene (as shown in Fig. 8) nor by the addition of cyclohexene. Similar results were obtained with 1,4-CHD. These results indicate that adsorptions of CHD and butadiene are competitive, as are the reactions of CHD and butadiene with hydrogen atoms released from CHD.

In order to deduce a relative adsorption strength on the CoS catalyst, the isomerization of 1-butene was performed in the presence of CHD, benzene, or cyclo-

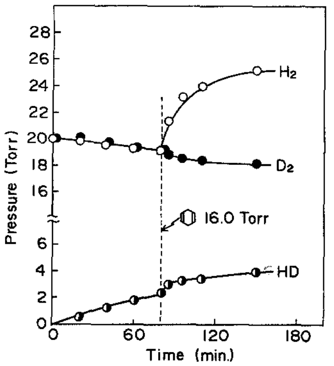


FIG. 6. Effect of 1,4-CHD addition on H_2–D_2 equilibration over CoS at 240°C.

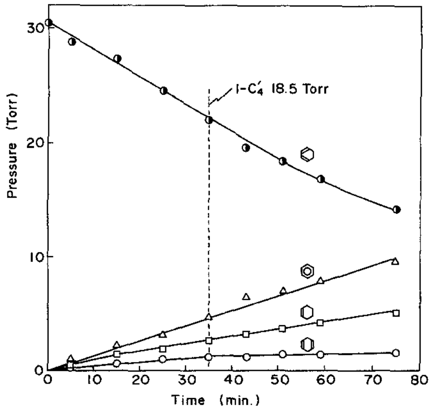


FIG. 8. Effect of 1-butene addition on the reaction of 1,3-CHD over CoS at 240°C.

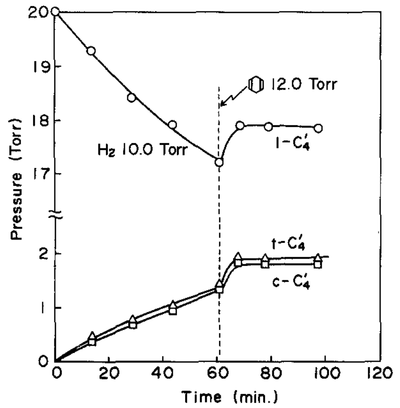


FIG. 9. Effect of 1,4-CHD addition on the reaction of 1,3-CHD over CoS at 240°C.

hexene. The isomerization reaction was retarded by CHD and benzene as shown in Figs. 9 and 10, respectively, but was not inhibited by cyclohexene. Figure 9 shows a rapid displacement of adsorbed butene by CHD and complete inhibition of butene isomerization. On the basis of these results, the sequence of adsorption strength on CoS may be described as follows:

$$\text{Butadiene} \cong \text{CHD} > \text{benzene} > \text{butene} > \text{cyclohexene}. \quad (1)$$

Isomerization of 1,3-CHD to 1,4-CHD took place without hydrogen, as shown in Fig. 7, distinctly differing from isomerization of 1-butene, for which the coexistence of hydrogen is necessary (Fig. 10).

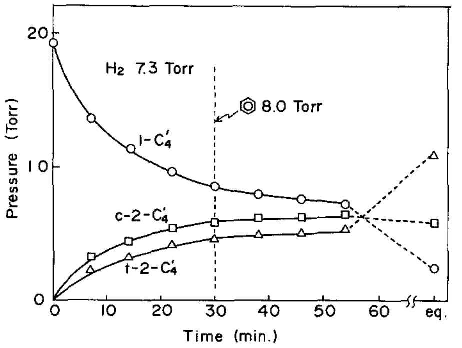


FIG. 10. Effect of benzene addition on the isomerization of 1-butene over CoS at 240°C.

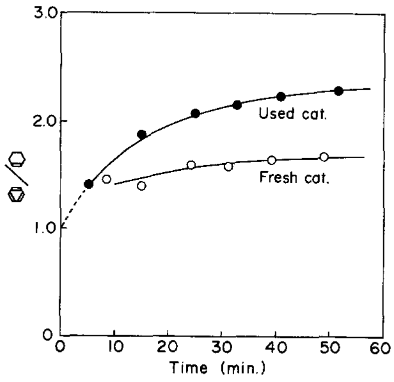


FIG. 11. Change of the amount ratio, benzene/cyclohexene, during the course of the reaction of 1,4-CHD over CoS at 240°C.

The catalyst was deactivated for the isomerizations of 1-butene as well as of 1,4-CHD by repetition of the reactions, but disproportionation of CHD was still taking place with preferential formation of benzene as shown in Fig. 11.

DISCUSSION

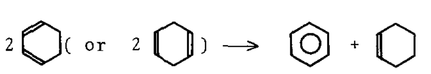
The results of the present work are summarized as follows.

1. CoS is inactive for catalytic hydrogenation of butadiene with hydrogen, but is active for the hydrogenation with CHD by hydrogen transfer reaction.
2. The hydrogenation of butadiene with CHD results in entire partial hydrogenation into butene, which is caused by the relative adsorption strength on CoS given by (1).
3. The apparent disproportionation reaction of CHD into benzene and cyclohexene takes place concurrently with the hydrogenation of butadiene. Benzene formation, which exceeds cyclohexene formation, and the different kinetics for these formations suggest that hydrogen atoms released from CHD onto the catalyst surface are competitively selected by butadiene and CHD, and partly transformed into gaseous hydrogen.
4. The results of Table 1 and Fig. 6 suggest considerably slow mixing between hy-

drogen atoms released from CHD and those of gaseous hydrogen.

The catalytic activity of CoS mentioned in result 1 above seems to be quite analogous to the catalytic activity of an Au film covering one side of a Pd–Ag film (*9*). Gold can adsorb olefin but not hydrogen (*10*) and, accordingly, is catalytically inactive for olefin hydrogenation. However, hydrogenation of cyclohexene took place on its surface using hydrogen atoms diffused through the Pd–Ag film from the opposite side. From the same point of view, we can understand the catalytic activity of Mo(CO)$_6$ (*11*) for refinement of crude petroleum and liquification of coal by the use of tetrarin, etc., as a hydrogen source.

The kinetic behaviors of the present reactions can be understood on the basis of the order of adsorption strength (*1*) as follows: The formation rate of benzene shown in Fig. 7 decreased to one-third by addition of butadiene in an amount half that of CHD, indicating that the adsorption strength of butadiene is slightly larger than that of CHD. Strong inhibition for formation of cyclohexene and 1,4-CHD is caused by the concurrent hydrogenation of butadiene which diminishes the amount of hydrogen atoms released from CHD. The ratio of benzene to cyclohexene should be unity when the disproportionation reaction predominates.



(2)

That was not the case, but the ratio was larger than unity and increased during the reaction of 1,4-CHD as shown in Fig. 11. This result may be explained by the adsorption of benzene which diminishes the amount of adsorbed CHD, a superior hydrogen acceptor, and accordingly, induces the evolution of hydrogen gas instead of cyclohexene. Figure 12 shows the effect of 1,4-CHD addition on the cyclohexene formation. It is obvious that the increase of adsorbed CHD results in more efficient cyclohexene formation. The apparent dependence of the formation rates of benzene and cyclohexene on CHD partial pressure (Fig. 4) observed in the course of the CHD disproportionation is understood from the same point of view as is the change in the amount of adsorbed CHD induced by the formation of benzene. The observed kinetics of the initial rates show that the catalyst surface is fully covered with CHD in the absence of benzene.

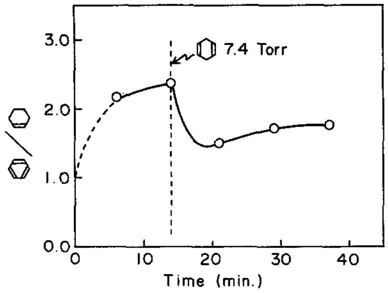


FIG. 12. Dependence of the amount ratio, benzene/cyclohexene, on 1,4-CHD pressure. The initial pressure of 1,4-CHD was 5.0 Torr.

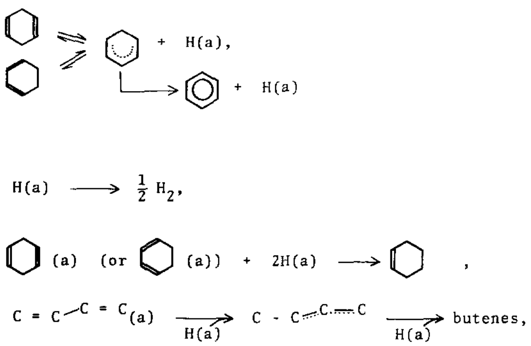
A mechanism in which hydrogen transferred from CHD to other molecules via adsorbed hydrogen atoms furnished from CHD may be supported by the identical selectivities for the hydrogenation of butadiene with 1,3- and 1,4-CHD, yielding 2-butene (Fig. 5). Direct hydrogen transfer from 1,3-, or 1,4-CHD to butadiene might yield 1- or 2-butene by 1,2- and 1,4-addition of hydrogen to the butadiene molecule, respectively. The random distribution of deuterated butene in the reaction of butadiene with CHD in the presence of D$_2$ also indicates the reaction with dissociated hydrogen atoms from CHD (Table 1). A small amount of deuterated butenes may be formed through slow Rideal–Eley type substitution of hydrogen atoms by deuterium as

$$\mathrm{H(a)} + \mathrm{D_2} \rightarrow \mathrm{D(a)} + \mathrm{HD},$$

which ensures the random distribution of D atoms in butene.

In contrast with the hydrogenation of butadiene on ZrO_2, where the reaction with H_2 and 1,3-CHD yielded different products, 2-butene and 1-butene, respectively (*12*), CoS had no catalytic activity for the hydrogenation reaction with gaseous hydrogen, and the reaction with 1,3- or 1,4-CHD gave 2-butene selectively (Fig. 5).

The discussions above can be summarized with respect to the reaction mechanism as



where a one-directional arrow indicates a step practically irreversible because of the order of adsorption strength (*1*).

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