Study on the Selective Hydrogenation of Butadiene in C₄-Hydrocarbon Fraction (Part 1)*

—Removal of Butadiene over Palladium-Alumina Catalyst—

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Summary: Selective hydrogenation of butadiene to remove the butadiene from C₄ hydrocarbon fraction has been studied over palladium-alumina catalyst at elevated pressure. The following results were obtained.

- (1) Presulfiding of the catalyst and presence of sulfur compounds in the reaction system were required to increase the selectivity of hydrogenation when butadiene content in C₄ fraction was relatively high (>1.0%).
- (2) It was found to be effective that presulfiding of the catalyst by hydrogen sulfide was carried out under low temperature in order to gain high hydrogenation selectivity.
- (3) Complete removal of butadiene without *n*-butenes loss was achieved from the studies on the reaction conditions. Activity and selectivity of the catalyst were preserved constantly during long run test.
- (4) Isomerization of 1-butene accompanied with hydrogenation was retarded by the presence of butadiene. Complete isomerization of 1-butene to 2-butene needed more severe conditions than complete removal of butadiene hydrogenation.
- (5) Palladium-alumina catalyst sulfided by hydrogen sulfide showed relatively strong resistance against the poison. In the presence of some gaseous inorganic compounds such as CO, Cl₂, COCl₂, N₂O, N₂O₃, and SO₂, selectivity of the hydrogenation increased. Moreover, CO completely depressed the isomerization of 1-butene.

1 Introduction

Butadiene contained in C₄-hydrocarbon fraction, even in a small quantity, has a harmful effects on petrochemical manufacturing processes which utilize *n*-butenes and isobutene in C₄ fraction.

Selective hydrogenation is preferred to eliminate butadiene from C₄ fraction. Although many reports have been published on the selective hydrogenation of butadiene over various catalysts such as noble group VIII metals^{1)~7)}, nickel-kieselguhr^{8)~10)}, and zinc oxide¹¹⁾, a little study on the removal of small quantity of butadiene from C₄ fraction by selective hydrogenation has been done. Kirsch and Shull¹²⁾ removed butadiene from C₄ fraction by hydrogenation over sulfided cobalt-molybdena catalyst and Tomihisa et al.^{13),14)} studied the removal of butadiene from the town gas over the same catalyst. Kroenig¹⁵⁾ removed butadiene by the

low temperature liquid phase hydrogenation over palladium-alumina catalysts, but these catalysts were too sensitive to the poisonous material such as sulfur compounds and carbon monoxide. Takahashi et al.¹⁶⁾ studied the hydrogenation of butadiene in C₄ fraction over palladium-alkali-alumina catalysts under atmospheric pressure.

In the present work, the selective hydrogenation of butadiene in C₄ fraction has been carried out at elevated pressure over palladium-alumina catalyst in the presence of sulfur compounds, and the effects of presulfiding of the catalyst, reaction conditions and some organic and inorganic compounds added have been investigated.

2 Experimental

2.1 Apparatus and Procedure

2.1.1 Autoclave Test

An autoclave of 500 ml capacity equipped with a magnetic stirrer, sampling tube and electronic furnace was used.

The weighed amount of powdered catalyst (through 150 mesh) was charged into the auto-

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Fig. 1 Flow Diagram of Experimental Apparatus

clave from which the air was replaced by dry hydrogen gas. Liquid C_4 fraction was charged into the autoclave. The amount of C_4 fraction was measured by reading the scale of the liquid feeder.

When the temperature of the contents of the autoclave reached to the reaction temperature, stirring was started and the hydrogen gas was introduced to the desired pressure. The reaction was assumed to start at this point. If necessary, samples of reaction mixture were taken out at the desired reaction time.

After reaction, the contents of the autoclave was transferred into a receiver in a dry ice-acetone bath. The non-condensable gas (mainly hydrogen) was collected in gas holder connected to the receiver.

2.1.2 Bench Scale Test

The experiments were carried out in a flow system at elevated pressure. A flow diagram of the apparatus is shown in **Fig. 1**. The reactor used was a SUS 32 tube of 30 mm inside diameter and 1,000 mm length. The temperature of the catalyst bed was measured by an alumel-chromel thermocouple.

C_4 fraction was charged to the bottom of the reactor through preheater. The flow velocity of C_4 fraction was controlled by feed pump and measured by reading the scale of the C_4 vessel. Hydrogen gas was charged to the reactor together with C_4 fraction. The flow velocity of hydrogen gas was measured by a high pressure

Table 1 Typical Composition of C_4 Fraction

Butadiene (ppm)	22,760	2,336
1-Butene (mol%)	25.1	24.7
<i>trans</i> -2-Butene (mol%)	13.8	10.4
<i>cis</i> -2-Butene (mol%)	8.8	7.0
Isobutene (mol%)	43.1	45.1
Butanes (mol%)	6.2	11.8
Sulfur (ppm)	< 5	< 5

gas flow meter. The product from the top of the reactor was separated in a separator to C_4 fraction and hydrogen.

2.2 Catalyst

The palladium-alumina catalyst used (pellet of 1/8 inch diameter and 1/8 inch height) was supplied by Nippon Engelhard Co., Ltd. This catalyst was prepared by the impregnation method¹⁷⁾. The amount of palladium on this catalyst was 0.1% and the BET area was 95 m²/g-cat.

2.3 Materials

C_4 fraction used was a product of naphtha cracking from which most of butadiene had been removed by extraction. Residual butadiene in C_4 fraction was about 2,000 ppm to 3%. Typical composition of C_4 fraction is shown in **Table 1**. Hydrogen was purchased in cylinder. Both C_4 fraction and hydrogen were used without further treatment. Organic and inorganic compounds were GR or EP grade reagents and were used without further treatment.

2.4 Analysis

C₄ fraction was analyzed using a gas chromatograph with a columns of 0.2×600 cm packed with β,β'-ODPN (30 wt%) on chromosorb P (70 wt%, 60 to 80 mesh) plus 0.2×300 cm packed with β,β'-ODPN (1 wt%) on Durapack (n-octane/Porasil C, 80 to 100 mesh). The carrier gas was N₂ (3.4 kg/cm²·G input pressure) and the column temperature was 25°C. FID detector was used.

3 Results and Discussions

3.1 Effects of Butadiene Contents in C₄ Fraction

When butadiene content in C₄ fraction was relatively low (<1%), as shown in Fig. 2, butadiene was selectively hydrogenated with a little *n*-butene loss at low temperature (50°C) in the absence of sulfur compounds. Isomerization of 1-butene was observed only under the condition in which the removal of butadiene was possible. Activity of hydrogenation was proportional to that of isomerization. As the content of butadiene increased, shown in Fig. 3, selectivity of hydrogenation decreased and *n*-butene loss by hydrogenation increased under the condition in which butadiene was removed.

3.2 Hydrogenation in the Presence of Sulfur Compounds

Hydrogen sulfide (H₂S) was added in order to obtain high selectivity in the hydrogenation of butadiene in C₄ fraction in which high content

Temp.=50°C, Pressure=15 kg/cm²·G, LHSV=6
Feed: *n*-Butenes 44.7%, 1-Butene 26.3%,
Butadiene 1,860 ppm

Fig. 2 Hydrogenation of Butadiene in the Absence of Sulfur Compound

of butadiene (1 to 3%) was contained. Results are shown in Fig. 4. At the suitable amount of H₂S, butadiene was removed less than 100 ppm with little *n*-butenes loss. H₂S served to raise selectivity more effectively by adding in C₄ fraction than adding in hydrogen. It was assumed from these results that H₂ and H₂S in the liquid phase more effectively participate to the hydro-

Temp.=50°C, Pressure=15 kg/cm²·G, LHSV=6
Feed: *n*-Butenes 40.2%, 1-Butene 25.1%,
Butadiene 2.8%

Fig. 3 Hydrogenation of Butadiene in the Absence of Sulfur Compound

Temp.=100°C, Pressure=35 kg/cm²·G, LHSV=3
H₂/Butadiene mole ratio=20~23
Feed: *n*-Butene 40.3%, 1-Butene 25.5%,
Butadiene 2.2%

Fig. 4 Effects of Amount of H₂S Added

generation reaction than in the gas phase.

Various mercaptan compounds and H₂S showed almost the same effects as given in **Table 2**.

Fig. 5 shows the plot of the content of butadiene, 1-butene and 2-butene, and the ratio of *trans*-isomer/*cis*-isomer in formed 2-butene by isomerization against reaction time. Isomerization of 1-butene was retarded while butadiene

Table 2 Effects of Sulfur Compounds (Autoclave Test)

Reaction conditions:

Temp.=100°C Catalyst=10 vol%

Pressure=25 kg/cm²·G Time=2 hr

Sulfur Compound*	Product Composition		n-Butenes Loss (%)
	Butadiene (ppm)	1-Butene (%)	
H ₂ S	25	2.1	4.0
CH ₃ SH	22	2.1	3.2
C ₂ H ₅ SH	<10	1.8	2.3
n-C ₃ H ₇ SH	<10	2.2	3.0
n-C ₄ H ₉ SH	<10	1.8	3.5
i-C ₄ H ₉ SH	22	2.1	3.0
sec-C ₄ H ₉ SH	18	2.0	4.0
tert-C ₄ H ₉ SH	<10	1.9	3.7
Feed	19,300	26.0	—

* Added 100 ppm as S in C₄ fraction.

Temp.=100°C Pressure=25 kg/cm²·G
Catalyst=5 wt% H₂S=250 ppm (in C₄)

Fig. 5 Relationships between Reaction Time and Product Composition

remained in C₄ fraction. The ratio of *trans*-isomer/*cis*-isomer in formed 2-butene increased toward the equilibrium in which the ratio of *trans*-isomer/*cis*-isomer¹²⁾ was 2.6 with reaction time. Therefore, *trans*-isomer/*cis*-isomer ratio of 2-butene which formed initially from 1-butene seemed to be lower value. It was assumed from these results that 1-butene isomerization proceeded through the addition-abstraction mechanism¹⁸⁾ in which the distribution of 2-butene isomers during the initial portion of the isomerization was of equal magnitude and equilibrium distribution of the 2-butene isomers was ultimately attained by subsequent interconversion of *cis*- and *trans*-2-butene.

3.3 Presulfiding of the Catalyst

3.3.1 Presulfiding Condition

Presulfiding of the catalyst was carried out in the reactor at atmospheric pressure by the H₂S-hydrogen gas mixture which contains about 4,000 ppm of H₂S. After the presulfiding, the catalyst was used to the hydrogenation reaction without taking out of the reactor. **Fig. 6** shows the

Hydrogenation conditions:

Temp.=100°C Pressure=25 kg/cm²·G

LHSV=3 H₂/Butadiene mole ratio=20

H₂S=100 ppm (in C₄ fraction)

Time on stream=2~4 hr

Fig. 6 Effects of Temperature and Amount of H₂S Added in Presulfiding

effects of temperature and amount of sulfur added to the catalyst in presulfiding on the hydrogenation reaction. Activity of the butadiene hydrogenation decreased by less added H_2S in the higher temperature presulfiding. On the other hand, selectivity of hydrogenation was found to be better in the lower temperature presulfiding. Thus, at the same residual butadiene, for example 100 ppm, higher *n*-butenes content was obtained at 25°C presulfiding (*n*-butenes content $\approx 39\%$) than at 100°C presulfiding (*n*-butenes content $\approx 38\%$). The similar results were obtained in the presulfiding by H_2S -hydrogen gas mixtures of 1,500 ppm and 7,000 ppm of H_2S . It was found to be effective that presulfiding of the catalyst by hydrogen sulfide was carried out under low temperature in order to gain high hydrogenation selectivity.

3.3.2 Deactivation by Over-Presulfiding and Reactivation

Hydrogenation activity decreased with the increase of the amount of added H_2S to the catalyst in presulfiding and the catalyst completely lost the activity over S/Pd atomic ratio 35~40.

In order to reactivate the catalyst which lost the activity, the catalyst was treated by hydrogen

Table 3 Reactivation in Hydrogen

Reaction conditions:
Temp. = 70°C Pressure = 15 kg/cm²·G
 $\text{H}_2/\text{C}_4\text{H}_6$ mole ratio = 2.0 LHSV = 3.0
 H_2S in C_4 = 100 ppm
Butadiene in raw C_4 fraction = 22,000 ppm

Reactivation Condition		Butadiene after Hydrogenation (ppm)
Temperature (°C)	Time (hr)	
—	—	19,000
10	16	17,200
30	8	15,800
40	8	268
50	8	224

Table 4 Reactivation under Hydrogenation Condition

Reaction conditions:
Temp. = 100°C Pressure = 25 kg/cm²·G
LHSV = 3 $\text{H}_2/\text{C}_4\text{H}_6$ mole ratio = 20
 H_2S in C_4 = 100 ppm

Time on Stream (hr)	Product Composition		<i>n</i> -Butenes Loss (mol%)
	Butadiene (ppm)	1-Butene (mol%)	
4	4,120	23.0	+2.2
8	497	15.5	+0.5
12	129	12.0	-0.2
16	152	12.2	+1.7
20	136	12.3	-1.2
Feed	19,200	25.9	—

at atmospheric pressure. As shown in **Table 3**, the activity was reproduced by the hydrogen treatment with the condition in which temperature was higher than 40°C and time was over 8 hours. **Table 4** shows the results of the reactivation of the catalyst in the hydrogenation condition. The activity was gradually restored with time on stream, and high activity and selectivity were attained after 12 hours.

These reactivation data show that the catalyst activity lost by the addition of H_2S was restored readily even in the case of complete deactivation by over-presulfiding.

3.4 Effects of Reaction Conditions

Reaction conditions of the hydrogenation in the presence of H_2S were studied. Catalyst presulfiding conditions were as follows: H_2S concentration in H_2S -hydrogen gas mixture = 4,000 ppm, temperature = 25°C, atomic ratio of S/Pd = 4.0. By these presulfiding conditions the steady results were obtained after 1 hr from the start of the hydrogenation reaction.

3.4.1 Reaction Temperature

Optimum reaction temperature range was 80°C to 120°C, as shown in **Table 5**. In this range 1-butene was isomerized to 2-butene nearly in equilibrium. Both the hydrogenation and the isomerization activity was slight at lower temperature than 45°C.

3.4.2 Reaction Pressure

Table 6 shows the influences of the pressure. Under low pressure (5 kg/cm²·G) hydrogenation activity was low. High activity and selectivity were obtained under high pressure (15 kg/cm²·G), but liquid phase in the reaction system was not necessarily desired.

3.4.3 Hydrogen/Butadiene Ratio and LHSV

Table 5 Effects of Temperature

Reaction conditions:
Pressure = 35 kg/cm²·G LHSV = 3
 $\text{H}_2/\text{C}_4\text{H}_6$ mole ratio = 20 H_2S in C_4 = 100 ppm

Temperature (°C)	Product Composition*		<i>n</i> -Butenes Loss (%)
	Butadiene (ppm)	1-Butene (%)	
15	26,000	24.4	0.0
45	23,000	24.2	0.0
60	1,630	18.5	0.0
80	50	3.6	1.2
100	35	3.4	2.5
120	45	4.0	2.2
150	20	3.2	7.5
Feed	35,000	24.6~25.7	—

* Time on stream = 2~4 hr.

Table 6 Effects of Pressure

Reaction conditions: Temp.=100°C, LHSV=3, H₂S in C₄=100 ppm

Pressure (kg/cm ² .G)	H ₂ /Butadiene Mole Ratio	Product Composition*		n-Butenes Loss (%)	State of C ₄ in Reaction System Vapor (wt%) Liquid (wt%)
		Butadiene (ppm)	1-Butene (%)		
5	10	6,500	24.9	0.3	100/0
5	15	3,200	24.8	0.5	"
5	21	3,300	24.5	0.2	"
15	11	550	12.2	0.5	"
15	20	58	5.5	0.1	"
15	28	50	5.6	0.8	"
35	10	420	5.8	0.1	11/89
35	18	47	6.2	0.5	24/76
35	29	55	4.8	0.7	38/62
Feed		28,100	25.5	—	—

* Time on stream=2~4 hr.

Temp.=100°C Pressure=15 kg/cm².G
H₂S=100 ppm (in C₄ fraction)
Time on stream=2~4 hr
Feed: n-Butenes 40.5%, 1-Butene 25.8%,
Butadiene 3.0%

Fig. 7 Effects of H₂/Butadiene Mole Ratio and LHSV

Butadiene was completely removed in the range of LHSV 3 to 6 and H₂/butadiene mole ratio 20, as shown the Fig. 7, and 1-butene isomerized closely to the equilibrium only at LHSV 3. These results showed that complete isomerization of 1-butene to 2-butene needed more severe conditions than complete removal of butadiene by hydrogenation.

Hydrogen/butadiene ratio affected largely to the rate of butadiene hydrogenation and 1-butene isomerization but did not to the selectivity of hydrogenation.

3.5 Long Run Test

As shown in Table 7, activity and selectivity were maintained constantly during the long run test. Furthermore, it was found from the results of the operation in the commercial plant that the life of the catalyst till regeneration was 1 to 2 years and varied with butadiene content in the raw C₄ fraction, and the decrease of activity was caused by the carbon deposit on the catalyst surface and the activity was restored by the regeneration in which carbon deposit was burned with air.

3.6 Hydrogenation in the Presence of Some Organic and Inorganic Compounds

The effects of organic and inorganic compounds on the hydrogenation in the presence of H₂S were investigated.

Table 8 shows the effects of organic compounds and water. Chloroform and tetrachloroethylene markedly decreased the activity of butadiene hydrogenation. In the presence of benzene, trichloroethylene and acetonitrile hydrogenation of butadiene and butenes occurred simultaneously. The activity of 1-butene isomerization was preserved in the presence of most of

Table 7 Long Run Test

Reaction conditions: Temp.=100°C, Pressure=15 kg/cm². G, LHSV=3, H₂/C₄H₆ mole ratio=20~25,
H₂S in C₄=100 ppm

Time on Stream	5		120		240		480	
	Charge	Product	Charge	Product	Charge	Product	Charge	Product
Composition								
Butadiene (ppm)	18,000	25.0	19,000	12.0	19,200	20.0	18,800	14.0
<i>n</i> -Butenes (mol%)	43.2	44.2	45.2	46.8	45.5	46.9	46.2	47.8
1-Butene (mol%)	27.5	4.1	25.8	4.3	26.2	3.8	25.4	4.4
<i>n</i> -Butenes Loss (mol%)	0.7		0.4		0.4		0.5	

Table 8 Effects of Organic Compounds and Water (Autoclave Test)

Reaction conditions:
Temp.=100°C Pressure=25 kg/cm². G
Catalyst=10 vol% Time=2 hr
H₂S in C₄=100 ppm

Compound*	Product Composition (%)		
	Butadiene (ppm)	<i>n</i> -Butenes Total	1-Butene
—	39	39.3	2.5
<i>n</i> -Hexane	<10	39.2	2.0
Benzene	<10	13.9	0.8
Methyl alcohol	56	38.0	2.7
<i>sec</i> -Butyl alcohol	<10	29.7	1.4
Methyl ethyl ketone	41	39.5	2.7
Tetrahydrofuran	<10	39.9	2.0
Isobutylaldehyde	<10	38.3	8.9
Dichloromethane	<10	33.6	1.9
Chloroform	18,000	41.3	25.5
Carbontetrachloride	72	29.9	1.7
Trichloroethylene	47	18.4	0.8
Tetrachloroethylene	6,000	41.6	23.3
Ethylenediamine	61	38.3	13.2
<i>N,N</i> -Dimethylformamide	183	38.6	4.4
Acetonitrile	27	21.0	1.1
Ethylene glycol	57	39.4	7.5
Water	<10	22.0	1.2
Feed	19,000	41.8	25.9

* Amount of addition: 16 vol% (based on liquid C₄)

Table 9 Effects of Metal Compounds (Autoclave test)

Reaction conditions:
Temp.=100°C Pressure=25 kg/cm². G
Catalyst=10 vol% Time=2 hr
H₂S in C₄=100 ppm

Compound (ppm)	Product Composition (%)		
	Butadiene (ppm)	<i>n</i> -Butenes Total	1-Butene
—	39	39.3	2.5
CH ₃ COONa	1,000	35	37.8
(C ₆ H ₅) ₃ P	100	17,000	41.6
KAsO ₂	10	<10	12.6
KSeO ₃	10	<10	9.0
K ₂ TeO ₃	10	<10	17.0
CH ₃ COOAg	1,000	<10	6.1
Zn(CH ₃ COO) ₂	1,000	15	16.8
Zn(C ₁₈ H ₃₅ O ₂) ₂	1,000	20	37.1
Hg(CH ₃ COO) ₂	1,000	38	22.5
Pb(CH ₃ COO) ₂	1,000	<10	7.4
Pb(C ₁₈ H ₃₅ O ₂) ₂	1,000	<10	2.3
Cu(CH ₃ COO) ₂	1,000	43	39.4
Feed	19,000	41.8	25.9

Table 10 Effects of Inorganic Gaseous Compounds (Autoclave Test)

Reaction conditions:
Temp.=100°C Pressure=25 kg/cm². G
Catalyst=10 vol% Time=2 hr

Compound (mol% in H ₂)	Product Composition (%)		
	Butadiene (ppm)	<i>n</i> -Butenes Total	1-Butene
—	<10	2.5	0.2
H ₂ S	100 (ppm)	30	34.8
CO ₂	28	63	17.8
CO	11	<10	37.8
"	28	<10	37.0
Cl ₂	28	281	35.7
COCl ₂	28	48	35.5
NOCl ₂	11	46	20.6
NO ₂ Cl	11	<10	31.6
N ₂ O	28	96	35.3
N ₂ O ₃	28	71	33.6
NO	7	78	26.5
NH ₃	28	91	24.9
SO ₂	7	43	34.0
HCN	7	77	28.4
PH ₃	7	39	10.8
SiH ₄	28	27	27.2
Feed	19,000	37.0	25.1

the organic compounds which did not decrease the hydrogenation activity except ethylenediamine which gave a little depression of 1-butene isomerization. Water did not affect the activity of butadiene hydrogenation and 1-butene isomerization, but lowered the hydrogenation selectivity.

Table 9 shows the effects of metal compounds. Triphenyl phosphine completely inhibited the hydrogenation activity. Some metal compounds such as potassium arsenite, potassium selenite, potassium tellurite, silver acetate, lead acetate and lead stearate accelerated both the hydrogenation of butadiene and butenes, consequently the hydrogenation selectivity decreased.

It was found from these data that palladium-alumina catalyst which was treated with H₂S had relatively strong resistance against the poisonous materials in the hydrogenation conditions.

The effects of inorganic gaseous compounds which were added instead of H₂S were studied. As shown in **Table 10**, all compounds tested here scarcely affected the activity, but increased the selectivity. Especially, CO, Cl₂, COCl, N₂O, N₂O₃ and SO₂ showed the same effects of increasing the selectivity as H₂S. Moreover, CO completely depressed the 1-butene isomerization, and Cl₂ and N₂O did a little.

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