

# Studies on Hydrogenation Reactions with Metal Sulfide Catalysts. III. Hydrogenation and Isomerization of Cyclohexene\*<sup>1</sup>

King HAI CHANG

Laboratory of Synthetic Organic Chemistry, Faculty of Science and Engineering,  
Nihon University, Surugadai, Chiyoda-ku, Tokyo

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The catalytic liquid phase hydrogenation and/or isomerization of cyclohexene are investigated at 160—350°C under 50—90 kg/cm<sup>2</sup> of hydrogen or atmospheric nitrogen using molybdenum trisulfide and various other metal sulfides or oxides, with or without additives, as catalysts. The activity of catalysts is found to be in the order of  $\text{MoS}_3 \geq \text{MoS}_2 > \text{WS}_3 > \text{CoS}_3 > \text{NiS}_2$ . The hydrogenation product is almost entirely cyclohexane, except when molybdenum trisulfide is used as a catalyst, in which case the reaction at 310°C accompanies isomerization to a considerable extent, yielding up to 24% of methylcyclopentane. The molybdenum disulfide catalyst with the addition of sulfur or hydrogen sulfide is similar to the molybdenum trisulfide in its selectivity for the course of reaction. The reason for these results is discussed. The main isomerization reaction path is found to be cyclohexene  $\rightarrow$  methylcyclopentene-(1)  $\rightarrow$  methylcyclopentane.

There have hitherto been many reports on the catalytic hydrogenation of cyclohexene. However, there are few studies on the activity and selectivity of molybdenum sulfide catalysts in the hydrogenation of cyclohexene.

As stated in our previous studies,<sup>1,2)</sup> the hydrogenation activity of the molybdenum trisulfide catalyst is considerably higher than that of other metal sulfide catalysts in many cases, and the extent of the formation of by-products due to the bond-cleavage through the hydrogenolysis of dodecanoic acid and related compounds is smaller for the molybdenum sulfide catalysts than for other metal sulfide and oxide catalysts.

In an attempt to determine the activity and selectivity of catalysts and the path of the isomerization reaction of cyclohexene, a series of experiments on the hydrogenation of cyclohexene with various metal sulfide and oxide catalysts under various conditions have been conducted in the present investigation.

## Experimental

**Materials.** Cyclohexene (bp 82.7—83°C,  $d_4^{20}$  0.8104,  $n_D^{20}$  1.446) was prepared from cyclohexanol by dehydration with sulfuric acid according to the procedure described by Coleman and Johnstone.<sup>3)</sup>

Cyclohexane, benzene and methylcyclopentane (bp

72—73°C,  $d_4^{20}$  0.751,  $n_D^{20}$  1.411) were of a guaranteed reagent quality supplied by the Tokyo Kasei Kogyo Co., Ltd.

Methylcyclopentene-(1) was prepared by the following method: methylcyclopentanol-(1), prepared from cyclopentanone and methyl iodide by the Grignard reaction,<sup>4)</sup> was dehydrated with dimethylsulfoxide at 160°C for 6 hr, and then distilled<sup>5)</sup> (bp 75—76°C,  $d_4^{20}$  0.772,  $n_D^{20}$  1.433).

**Preparation of Catalysts.** Six different catalysts were prepared following the methods previously reported.<sup>1,2)</sup> The silica-alumina catalyst (alumina content: 50% by weight) was, however, supplied by the Nikki Chemical Co., Ltd. The catalysts may be classified into two types, *i.e.*, the metal sulfide catalysts, such as molybdenum, nickel, cobalt and tungsten sulfides, and the metal oxide catalysts, such as molybdenum oxide and silica-alumina.

**Reaction Vessel.** An autoclave of 200-ml capacity with an electromagnetic stirrer which is able to produce reciprocal motion vertically, was used as the vessel for hydrogenation.

**Activity of Catalyst.** Hydrogenation activity was measured by the hydrogen uptake in the course of 100 min.

**Hydrogenation Reaction.** A 16.43 g portion (0.2 mol) of cyclohexene with 0.01—0.03 mol of a catalyst, with or without additives, was hydrogenated at the desired temperature under an initial pressure of 95 kg/cm<sup>2</sup>.

**Isomerization Reaction.** A 16.43 g portion (0.2 mol) of cyclohexene was heated at various temperatures under an initial pressure of 50 kg/cm<sup>2</sup> of hydrogen or atmospheric nitrogen in the presence of a catalyst.

**Separation and Determination of Products.** The reaction product in the autoclave was washed out with

\*<sup>1</sup> This work was presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) Part I: K. H. Chang and K. Itabashi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 63 (1966).

2) Part II: K. H. Chang, *ibid.*, **69**, 1160 (1966).

3) G. H. Coleman and H. F. Johnstone, *Org. Synth. Coll. Vol. I*, p. 183 (1956).

4) N. Zelinsky and S. Namjetkin, *Ber.*, **35**, 2683 (1902).

5) V. J. Traynelis, W. L. Hergenrother, H. T. Hansen and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964).

TABLE 1. THE HYDROGENATION OF CYCLOHEXENE WITH VARIOUS METAL SULFIDE CATALYSTS\*

Expt. No.	Catalyst	Reaction temp. °C	Apparent H <sub>2</sub> absorption mol	Product wt. g	Yield, %		
					Cyclohexane	Methylcyclopentane	Recovered cyclohexene
1	MoS <sub>3</sub>	160	0.01	0.44	2.3	Trace	97.5
2	MoS <sub>3</sub>	200	0.09	7.82	44.2	2.5	53.1
3	MoS <sub>3</sub>	220	0.12	10.10	54.2	6.0	40.2
4	MoS <sub>3</sub>	250	0.17	14.30	71.5	13.5	14.0
5	MoS <sub>3</sub>	310	0.20	16.11	72.1	24.0	4.2
6	WS <sub>3</sub>	220	<0.01	0.36	1.9	Trace	98.0
7	WS <sub>3</sub>	250	0.07	5.62	32.5	1.1	67.0
8	WS <sub>3</sub>	280	0.18	15.52	90.0	2.0	8.1
9	WS <sub>3</sub>	310	0.19	16.10	90.5	5.2	4.5
10	MoS <sub>2</sub>	160	<0.01	0.34	1.5	Trace	98.0
11	MoS <sub>2</sub>	200	0.08	6.71	40.2	0.5	59.1
12	MoS <sub>2</sub>	250	0.15	12.21	71.0	1.1	28.0
13	MoS <sub>2</sub>	280	0.19	15.71	91.5	2.1	6.2
14	CoS <sub>3</sub>	250	0.05	3.62	21.1	0.5	78.0
15	CoS <sub>3</sub>	280	0.08	7.06	41.0	1.0	58.0
16	NiS <sub>2</sub>	250	0.02	1.51	9.2	Trace	90.5
17	NiS <sub>2</sub>	280	0.03	2.18	13.1	Trace	86.5

\* Cyclohexene (0.2 mol) was hydrogenated with 0.01 mol of catalyst for 100 min under 95 kg/cm<sup>2</sup> initial hydrogen pressure.

ether, and freed from the catalyst by filtration. After the removal of the ether, the residue was distilled *in vacuo* by the use of a Vigreux fractionating column. The distillate and the distillation residue were then analysed by gas chromatography and by IR- and NMR-spectroscopy.

## Results and Discussion

**A Comparison of Catalysts in Their Activity and Selectivity.** As is shown in Table 1, cyclohexene was hydrogenated with each catalyst to yield cyclohexane as the main product, in an amount corresponding to the extent of apparent hydrogen absorption. Beside this main reaction, an isomerization reaction might have taken place, because methylcyclopentane was formed as a by-product. It is of interest that methylcyclopentane was produced in noticeable amounts only when the molybdenum trisulfide catalyst was used.

The hydrogen uptake during hydrogenation with each catalyst is shown in Fig. 1. When tri- or disulfide of molybdenum was used, the hydrogen uptake began to take place at 160°C, and it became rapid above 250°C. In the case of tungsten trisulfide, the lowest temperature to start the reaction was found to be 220°C, but the rate of reaction increased with increasing temperature becoming very rapid above 280°C. On the other hand, with the cobalt trisulfide and nickel disulfide catalysts, the hydrogen uptake was relatively small, even at a temperature as high as 280°C.

The activities of respective catalysts are found to

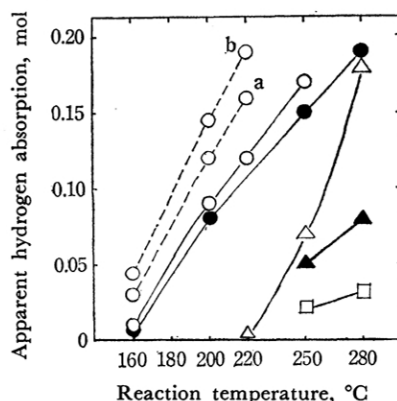


Fig. 1. Comparison of catalytic activities by plotting the apparent hydrogen absorption vs. reaction temperature.

○ MoS<sub>3</sub>, ● MoS<sub>2</sub>, △ WS<sub>3</sub>, ▲ CoS<sub>3</sub>, □ NiS<sub>2</sub>. Catalyst 0.01 mol for each, excepting 0.02 mol for the curve a and 0.03 mol for the curve b.

be as follows: MoS<sub>3</sub> ≥ MoS<sub>2</sub> > WS<sub>3</sub> > CoS<sub>3</sub> > NiS<sub>2</sub>.

Figure 2 shows the mole composition of each reaction product obtained in the above experiments. It may clearly be seen that the yields of methylcyclopentane with the use of a molybdenum trisulfide catalyst at 250°C and 310°C amount to 13.5% and 24%, respectively, suggesting that there is a tendency to a further increase in the yield at higher temperatures. On the contrary, the yield of cyclohexane showed almost no increase at these temperatures. As a result, the curve showing the mole

TABLE 2. THE EFFECT OF VARIOUS ADDITIVES ON SULFIDE CATALYSTS

Expt. No.	Catalyst*	Additive	mol	Apparent H <sub>2</sub> absorption mol	Product wt. g	Yield, %		
						Cyclohexane	Methylcyclopentane	Recovered cyclohexane
18	MoS <sub>3</sub>	Water	0.2	0.08	6.71	39.0	0.9	60.1
19	MoS <sub>3</sub>	Acetic acid	0.02	0.06	4.98	27.5	2.1	70.2
20	MoS <sub>3</sub>	NaOH + H <sub>2</sub> O	0.02 + 0.2	0.005	Trace	Trace	Trace	99.3
21**	WS <sub>3</sub>	Sulfur	0.02	0.03	0.66	3.9	Trace	96.0
22	MoS <sub>2</sub>	Sulfur	0.02	0.166	13.12	72.3	7.0	20.5
23	MoS <sub>2</sub>	Hydrogen sulfide	0.07	0.164	13.91	73.1	10.7	16.1

\* Catalyst (0.01 mol) was used for the hydrogenation of cyclohexene (0.2 mol) at 250°C for 100 min under initial hydrogen pressure of 95 kg/cm<sup>2</sup>.

\*\* At 220°C for 100 min.

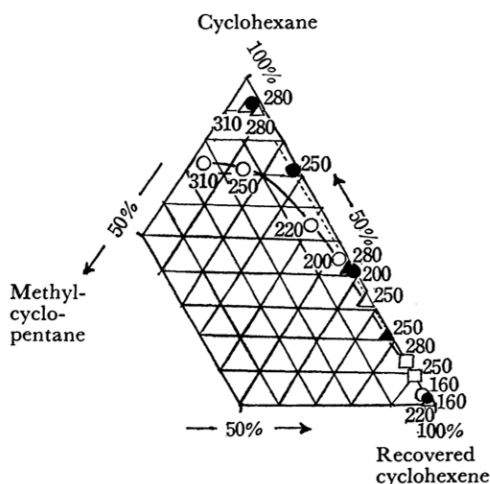


Fig. 2. Mol% compositions of hydrogenation products obtained with metal sulfide catalysts. Arabic numerals represent the reaction temperatures shown in Table 1.

○ MoS<sub>3</sub>, ● MoS<sub>2</sub>, △ WS<sub>3</sub>, ▲ CoS<sub>3</sub>, □ NiS<sub>2</sub>

composition versus the reaction temperature indicated a tendency to bend to the left, suggesting that it would curve downward to approach the point of the equilibrium between cyclohexane and methylcyclopentane at a certain elevated temperature.

There have been many reports on the hydrogenation-dehydrogenation function and the isomerization function of catalytic reforming catalysts,<sup>6)</sup> such as metallic platinum with silica-alumina or other metal oxide-alumina carriers.<sup>7)</sup> When cyclohexene is adsorbed on such a dual-function catalyst, a choice of hydrogenation and isomerization sites is available. It has also been reported that the iso-

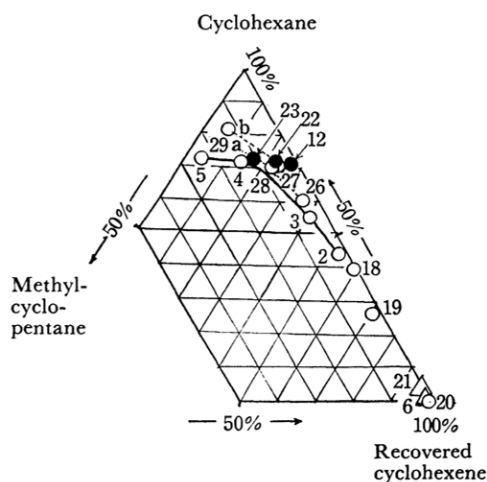


Fig. 3. The mol% composition change of hydrogenation products by the additives to the MoS<sub>2</sub> and WS<sub>3</sub> catalysts and by the amount of MoS<sub>3</sub> catalyst. Arabic numerals represent the Expt. Nos. shown in Tables 1, 2 and 3.

○, ●, △: 0.01 mol of MoS<sub>3</sub>, MoS<sub>2</sub> and WS<sub>3</sub>, respectively. Curves a and b: 0.02 mol and 0.03 mol of MoS<sub>3</sub>, respectively.

merization reaction can take place significantly at an elevated temperature of 450–500°C in the vapor phase with these dual function catalysts; however, with catalysts other than dual-function catalysts this reaction proceeds only to a 3–16% conversion,<sup>8)</sup> even under similar conditions.

As for metal sulfide catalysts, on the other hand, there has not been so much attention paid to the hydrogenation reaction of cyclohexene at elevated temperatures,<sup>9)</sup> and still less attention to the liquid phase reaction.

6) H. Heinemann, G. A. Mills, J. B. Hattman and F. W. Kirsch, *Ind. Eng. Chem.*, **45**, 130 (1953); F. G. Ciapetta, *ibid.*, **45**, 162 (1953).

7) V. Haensel and G. R. Donaldson, *ibid.*, **43**, 2102 (1951); H. Adkins and A. Roebuck, *J. Am. Chem. Soc.*, **70**, 4041 (1948).

8) G. A. Mills, H. Heinemann, T. H. Milliken and A. G. Oblad, *Ind. Eng. Chem.*, **45**, 134 (1953).

9) E. I. Prokopets and A. N. Filaretov, *Foreign Petroleum Tech.*, **7**, 199 (1939); *Chem. Abstr.*, **33**, 5817 (1939).

In the previous paper of this series it has been established that the activity of the molybdenum trisulfide catalyst for the hydrogenation of dodecanoic acid and related compounds is exceedingly higher than that of other metal sulfide catalysts; however, its activity for the isomerization reaction was left untouched. In this respect, the comparatively higher selectivity of the molybdenum trisulfide catalyst is of noteworthy. The reason for these results will be discussed later.

**The Effect of Additives.** The isomerization reaction by means of the molybdenum trisulfide catalyst are of considerable interest. Hence, the hydrogenation of cyclohexene was carried out using the molybdenum disulfide catalyst concurrently with sulfur or hydrogen sulfide as an additive and the results were compared with those obtained using molybdenum trisulfide catalyst. A series of hydrogenation experiments were also carried out using other additives, such as water, acetic acid, or sodium hydroxide (0.1 mol% aqueous solution), to the molybdenum trisulfide catalyst and a sulfur additive to the tungsten trisulfide catalyst. The results are shown in Table 2 and in Fig. 3.

As is obvious from Fig. 3, the conversion of cyclohexene was promoted by the use of sulfur as an additive to the molybdenum disulfide catalyst; however, the yield of cyclohexane remained at almost the same level with the case of the molybdenum disulfide catalyst alone, while, on the contrary, the isomerization reaction was then much more pronounced. Furthermore, in the presence of hydrogen sulfide as an additive to the molybdenum disulfide catalyst, the tendency to the isomerization reaction was even more significant.

On the other hand, the sulfur additive was found to exert no noticeable influence on the tungsten trisulfide catalyst at 220°C. The catalytic activities of molybdenum trisulfide catalysts were decreased by the addition of water and acetic acid, and almost disappeared upon the addition of a sodium hydroxide solution. It may be considered that the catalysts are partially poisoned by these additives. Particularly, molybdenum trisulfide is easy to dissolve in an alkali solution,<sup>10</sup> so that its catalytic activity may be lost. However, when acetic acid is used as an additive, the isomerization activity still remained partially, yielding a small amount of methylcyclopentane.

It is well-known that the molybdenum trisulfide catalyst is partially reduced to molybdenum disulfide<sup>11</sup> evolving a corresponding amount of hydrogen sulfide by the reaction of hydrogen under these con-

ditions.<sup>12</sup> The equilibria in the molybdenum-sulfur-hydrogen system was determined by Stubbles and Richardson.<sup>13</sup> In fact, the partial pressure of hydrogen sulfide involving in the equilibria of molybdenum sulfides should be taken into consideration in order to discuss the catalytic action of molybdenum sulfides. The molybdenum trisulfide catalyst employed contains sulfur in an excess of about 10% over the amount theoretically required for  $\text{MoS}_3$ ;<sup>14</sup> this catalyst was observed as amorphous by X-ray diffraction. After the use of this catalyst in the hydrogenation of cyclohexene, the catalyst was partially reduced into  $\text{MoS}_2$ , but it was still observed as amorphous. The activity of these catalysts is more pronounced than that of the natural molybdenite, which was determined to have a crystal form with the typical hexagonal layer lattice.<sup>10</sup>

**The Effect of the Amount of the Catalyst.**

The effect of the amount of molybdenum trisulfide catalyst on the hydrogenation reaction was determined at 200°C and at 220°C, with 0.01-, 0.02-, and 0.03-mol of the catalyst. The results are shown in Table 3. The relationship between the mole composition of the products and the reaction temperature for varying amounts of the catalyst is shown in Fig. 3.

As is obvious from Table 3 and Fig. 3, the yield of cyclohexane is improved by increasing the amount of catalyst even at the comparatively low hydrogenation temperatures. It may be conceived that the hydrogenation reaction is accelerated by an increase in the catalyst amount, thus enabling the hydrogenation to proceed smoothly at comparatively low temperature without accompanying the isomerization reaction to a considerable extent.

**On the Path of Isomerization.** In order to determine the path of the reaction, cyclohexene was heated at 250°C under an initial pressure of hydrogen of 50 kg/cm<sup>2</sup> in the presence of the molybdenum trisulfide catalyst, with or without additives, and oxide catalysts, such as silica-alumina and molybdenum oxide.

As is obvious from Table 4, the activities of the molybdenum oxide catalyst and the silica-alumina catalyst, which is often used as an acidic function catalyst, are very low under these conditions. The activity of the molybdenum trisulfide catalyst is found to fall to virtually null upon the addition of a concentrated solution of ammonium hydroxide.

However, a noteworthy result has been obtained with the addition of sulfur to the molybdenum trisulfide catalyst; the isomerization reaction was then clearly demonstrated by the formation of methylcyclopentene-(1) up to about 30%, accompanied by

10) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London (1931), pp. 640-650.

11) U. Colombo, I. Pasquon, J. B. McKinley, H. A. Smith, G. Natta, H. W. Sternberg, M. Orchin, T. I. Taylor and I. Wender, "Catalysis," Vol. V, ed. by P. H. Emmett, Reinhold Publishing Corporation, New York (1957), p. 454.

12) F. T. Eggertsen and R. M. Roberts, *J. Phys. Chem.*, **63**, [11] 1981 (1959).

13) J. R. Stubbles and F. D. Richardson, *Trans. Faraday Soc.*, **56**, Part 10, 1460 (1960).

14) K. Itabashi, *Yuki Gosei Kagaku Kyokaiishi (J. Synth. Org. Chem., Japan)*, **17**, 287 (1959).

TABLE 3. THE EFFECT OF THE AMOUNT OF CATALYST

Expt. No.	Amount of catalyst* mol	Reaction temp. °C	Apparent H <sub>2</sub> absorption mol	Product wt. g	Yield, %		
					Cyclohexane	Methylcyclopentane	Recovered cyclohexane
24	0.02	160	0.03	2.52	14.0	1.0	85.0
25	0.03	160	0.044	3.70	20.5	1.4	78.0
26	0.02	200	0.12	10.11	60.1	4.8	35.1
27	0.03	200	0.145	12.12	71.3	7.1	21.5
28	0.02	220	0.159	13.35	70.3	8.5	21.1
29	0.03	220	0.189	15.93	82.0	12.5	5.5

\* Molybdenum trisulfide catalyst was used for the hydrogenation of cyclohexene (0.2 mol) for 100 min under initial hydrogen pressure of 95 kg/cm<sup>2</sup>.

TABLE 4. THE HEAT TREATMENT OF CYCLOHEXENE IN THE PRESENCE OF CATALYSTS FOR ISOMERIZATION\*

Expt. No.	Catalyst	wt. g	Additive	wt. g	Apparent H <sub>2</sub> absorption mol	Methylcyclopentane	Methylcyclopentene	Cyclohexane	Benzene	Recovered cyclohexene
31	MoS <sub>3</sub>	1.9	—	—	0.08	0.4	Trace	47.1	—	52.0
32	MoS <sub>3</sub>	1.9	S	3.2	0.013	0.6	34.1	Trace	12.5	52.5
33	nil	—	—	—	~0	—	—	Trace	—	99.5
34	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1.6	—	—	0.02	—	1.2	1.8	—	96.4
35	MoO <sub>3</sub>	1.4	—	—	~0	—	0.3	Trace	—	99.5
36	MoS <sub>3</sub>	1.9	NH <sub>4</sub> OH (28% aq.)	3.5	0.002	0.4	1.4	Trace	—	98.0
40**	MoS <sub>3</sub>	1.9	—	—	—	0.7	15.8	2.5	15.6	64.6
41***	MoS <sub>3</sub>	1.9	—	—	—	3.2	31.1	2.9	17.5	45.1

\* Cyclohexene (0.2 mol) was used in each experiment. Expt. Nos. 31—36 were carried out at 250°C for 100 min under hydrogen pressure of 50 kg/cm<sup>2</sup>.

\*\* At 300°C for 60 min under atmospheric nitrogen.

\*\*\* At 350°C for 120 min under atmospheric nitrogen.

a trace of cyclohexane and about 10% of benzene. A similar result has been obtained from the heat treatment of cyclohexene with the molybdenum trisulfide catalyst under atmospheric nitrogen. It may be postulated that the reduction of sulfur and molybdenum trisulfide with hydrogen produces hydrogen sulfide, which then accelerates the isomerization reaction described above, whereas the dehydrogenation reaction might be promoted by the presence of sulfur under these conditions.

On the other hand, cyclohexane was found to be stable at 350°C under initial hydrogen pressures of 50—90 kg/cm<sup>2</sup>, irrespective of the presence or absence of the catalyst.

Although the formation of methylcyclopentene-(1) as well as methylcyclopentene-(2) in the vapor phase reaction at elevated temperatures with an alumina catalyst had been reported by Adkins *et al.*,<sup>7)</sup> the formation of methylcyclopentene-(1) as the main isomerization product in the liquid phase reaction at moderate temperatures is a new finding in present study.

In the vapor-phase conversion of cyclohexane to benzene and methylcyclopentane, or of methyl-

cyclopentane to benzene, over a platinum-alumina catalyst or over a platinum-alumina-halogen catalyst, the existence of methylcyclopentene, or of its equivalent as a carbonium ion, as an intermediate was successfully demonstrated by Haensel *et al.*<sup>7)</sup> In the multi-stage system, Cyclohexane (A)  $\rightleftharpoons$  Cyclohexene (A')  $\rightleftharpoons$  B  $\rightarrow$  C  $\rightleftharpoons$  Methylcyclopentene (D')  $\rightleftharpoons$  Methylcyclopentane (D), it is illustrated<sup>15)</sup> that A and D (saturated hydrocarbons) and their conjugated olefins, A' and D', are set up at the metallic function; A' is then transported ( $\rightarrow$ ) to the acidic function, where it is adsorbed as the carbonium ion B, then isomerized to the ion C and transported back to the metallic function as the olefin D'. In a normal dual-function catalyst, where the metallic and acidic functions are in close proximity, the equilibrium partial pressure of olefins is usually sufficient for the transport process not to be rate-limiting; hence, isomerization must be.

It was also reported by Haensel that, in the con-

15) G. C. Bond, "Catalysis by Metal," Academic Press, London and New York (1962), p. 444.

version of cyclohexane over a platinum-alumina catalyst at an elevated temperature, only 1–2% of methylcyclopentane was obtained. However, if a small amount of sulfur compounds was added to cyclohexane, methylcyclopentane and methylcyclopentene were obtained in amounts as large as 32–44% and 1–38%, respectively. This illustrated how the sulfur compounds poisoned the catalyst without changing the reaction mechanism; the methylcyclopentene intermediate existed long enough to undergo side reactions. The case of liquid phase reactions with the molybdenum trisulfide catalyst should, however, be explained somewhat different from the above, since the activity of this catalyst is believed not to be diminished by a sulfur additive,<sup>1)</sup> and since cyclohexene was used as the starting substrate in the liquid phase reaction in this study.

In accordance with the above conception, it may be proposed that the enhancement of the selectivity of molybdenum tri- and di-sulfide catalysts is probably due to the formation of new active sites on the surface of the catalysts under these hydrogenation conditions, since the equilibria in the molybdenum-sulfur-hydrogen system may exist and the surface of the catalysts may eventually be altered. It is clearly seen that the sulfur and hydrogen sulfide play important roles in the isomerization function of molybdenum sulfide catalysts under these conditions, but it needs a further study to give decisive conclusion as

to the nature of the surface of the catalysts.

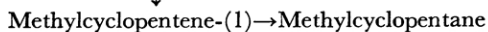
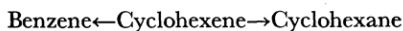
### Summary

(1) The activities and selectivities of various metal sulfide and oxide catalysts for the hydrogenation of cyclohexene have been compared.

(2) Upon the hydrogenation of cyclohexene with the molybdenum trisulfide catalyst, the accompanying isomerization reaction took place to a considerable extent. On the other hand, other catalysts showed scarcely isomerization function under similar conditions, except for the molybdenum disulfide catalyst with sulfur or hydrogen sulfide added.

(3) The hydrogenation-dehydrogenation and isomerization activities of the molybdenum trisulfide catalyst were determined by the heat treatment of cyclohexene under a relatively low pressure of hydrogen and atmospheric nitrogen.

The reaction path was determined as follows;



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