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The Effect of Oxidation State of Tungsten on Hydrocracking of *n*-Heptane over Tungsten Oxide

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Hydrocracking of *n*-heptane was investigated with tungsten oxide of various oxidation states under high pressure of hydrogen. It was found that the reaction products definitely change four times with changing oxidation state during the course of reduction of tungsten trioxide. In the presence of slightly reduced tungsten oxide WO_{3-a} ($WO_{2.84}$, tungsten oxide reduced at 445°C), isomerization and subsequent central cracking of *n*-heptane occurred predominantly, showing that the reaction proceeded by carbonium ion mechanism. As the oxidation state approaches tungsten oxide WO_{3-b} (WO_2 or $WO_{2+\alpha}$, tungsten oxide reduced at 500°C to 525°C), demethylation reaction to form methane and normal paraffins by the selective scission of terminal C–C bond took place predominantly. Further reduced tungsten oxide WO_{3-c} ($WO_{2-\beta}$, tungsten oxide reduced at 580–610°C) gave isomerized heptane and central cracked products as in the case of WO_{3-a}. Tungsten oxide WO_{3-d} reduced almost to tungsten metal above 680°C again favors demethylation rather than isomerization and central cracking. These results suggest that the oxidation state of tungsten determined the reaction mechanism of hydrocracking of *n*-heptane.

INTRODUCTION

The mechanism of hydrocracking with metal catalysts has been extensively studied by numerous investigators and it was confirmed that catalysts were effective either as metal (*1–15*) of nickel, cobalt, platinum, palladium and others, or as metal sulfides or oxides (*16–21*) of nickel, cobalt, molybdenum and tungsten.

The following two mechanisms have been proposed for the hydrocracking of paraffinic hydrocarbons. The first mechanism is a carbonium ion mechanism for platinum–alumina (*5*) and tungsten oxide–alumina (*21*) catalysts, where the reaction proceeds as follows:

$$n\text{-}C_7H_{16} \rightarrow \text{iso-}C_7H_{16} \rightarrow C_3H_8 + C_4H_{10} \rightarrow \ldots\ldots$$

The iso-/*n*- ratios of butane, pentane, and hexane of cracked products were reported to range from 1 to 4. The second mechanism is successive demethylation mechanism for metal catalysts of nickel and cobalt on alumina, silica, and silica–alumina, where the reaction proceeds as follows (*5, 8, 9, 12, 14*):

$$n\text{-}C_7H_{16} \rightarrow CH_4 + n\text{-}C_6H_{14} \rightarrow CH_4 + n\text{-}C_5H_{12} \rightarrow \ldots\ldots$$

The iso-/*n*- ratios of butane, pentane, and hexane of hydrocracked products by this mechanism were found to be very small, from 0.001 to 0.1.

Although the hydrocracking of paraffins with metallic nickel and cobalt was found to proceed by successive demethylation mechanism, the reaction with nickel- and cobalt-sulfides presumably proceeds by carbonium ion mechanism.

These facts suggest that the reaction mechanism changed possibly by the oxidation state or number and elements of ligands of metal. We wish to report that the catalysis of tungsten oxide for conversion reaction of *n*-heptane was determined in a very complicated way by the oxidation

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states of tungsten after hydrogen reduction of tungsten trioxide.

EXPERIMENTAL

Materials

n-Heptane was of pure grade (almost 100% by gas chromatography). Hydrogen was used after a purification by Deoxo unit containing palladium catalyst to remove trace amounts of oxygen and drying with a molecular sieve.

Catalysts

Tungsten trioxide was prepared by calcination of ammonium paratungstate $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$ at 550°C for 10 hr in air stream. Pure tungsten metal, kindly supplied by Nippon Inorganic Color and Chemical Co., was used.

Apparatus and Procedures

Hydrocracking was carried out in a flow system. Hydrogen was supplied from a high-pressure cylinder into the apparatus. *n*-Heptane was introduced quantitatively to the flow from a cylindrical pump. The gases were premixed and preheated prior to the reaction. The reactor was constructed from a stainless steel (SUS 32) tube of 400-mm length and 8-mm inside diameter. About 3.0 g (1.2 cc) of the catalyst from 80 to 100 mesh was packed at the middle of the reactor. A stainless steel sealed chromel–alumel thermocouple was placed at the center of the catalyst bed. The reaction was carried out at 440°C under 50 kg/cm^2, with LHSV 5.0, the initial ratio of $H_2/n\text{-}C_7H_{16}$ of 8, and the contact time of 30 sec (calculated under 50 kg/cm^2 at 0°C). The products were analyzed by gas-chromatographic units connected to the reactor. The chromatographic columns were packed with ethylbenzoate–dimethylsulfolane (1:1, 30 wt % on Chromosorb-P, 12 *M*) and Molecular sieve 13X (4 *M*), and helium and argon, respectively, were used as carrier gas.

RESULTS AND DISCUSSION

It is well known that the stability of carbonium ions decreases in the order, tertiary > secondary > primary > ethyl > methyl. If the conversion reaction of *n*-heptane proceeds by carbonium ion mechanism, it should produce large amounts of skeletally isomerized heptanes, propane, and butanes, along with small amounts of methane, ethane, pentanes, and hexanes. The hydrocracked products will show large values of the iso-/*n*- ratio. On the other hand, if the reaction proceeds by successive demethylation mechanism, the reaction products will indicate an opposite tendency, that is, a large amount of methane and *n*-hexane, and small amount of skeletally isomerized heptanes, propane, and butanes. Then, the ratios of iso-/*n*- will result in a smaller value.

Changes of Catalysis by Hydrogen Reduction of Tungsten Trioxide

The effects of reaction time on stream on hydrocracking of *n*-heptane with tungsten trioxide are shown in Fig. 1. The se-

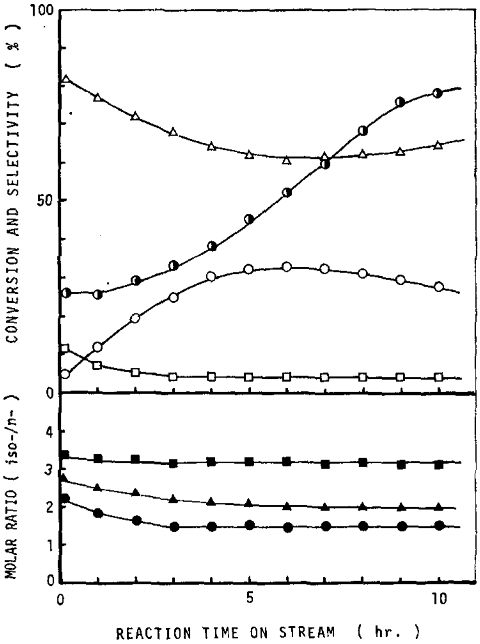
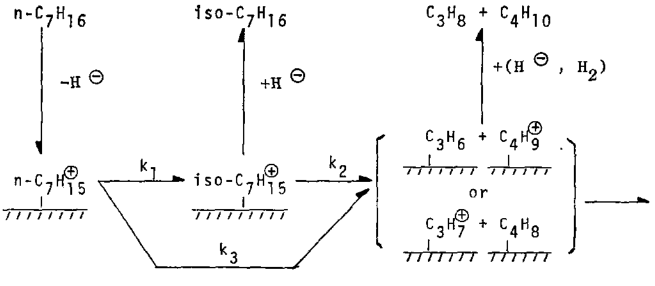


FIG. 1. Effect of reaction time on stream in hydrocracking of *n*-heptane over tungsten trioxide at 440°C, LHSV = 5, $H_2/n\text{-}C_7H_{16}$ = 8, and 50 kg/cm^2. ◑ conversion, ○ isomerized C_7H_{16}, △ $C_3H_8 + C_4H_{10}$, □ $CH_4 + C_2H_6 + C_5H_{12} + C_6H_{14}$, ● C_4H_{10}, ▲ C_5H_{12}, ■ C_6H_{14}.

lectivity for reaction products will be shown by carbon distribution throughout this work. The conversion increased proportionally with reaction time on stream. At initial time on stream, small amounts of carbon monoxide, carbon dioxide and olefins were produced, but decreased to negligible amounts after about 3 hr. These products should result from the oxidation and the oxidative dehydrogenation with oxygen of tungsten trioxide. The selectivities for methane, ethane, pentanes, and hexanes were very low, and those for skeletally isomerized heptanes and propane plus butanes in the hydrocracked products (centrally cracked products) as well as the ratios of iso-/*n*- for cracked products showed large values. The catalytic activity increased together with reaction time on stream. The total conversion increased from 20 to 78% after 10 hr, and to about 90% in 100 hr. The rate of increase in conversion decreased gradually. The relations of total conversion to selectivity at 420°C with tungsten oxide, after being used for 100 hr at 440°C, are shown in Fig. 2. At the initial stage, the isomerized heptanes were produced predominantly with 82% selectivity, and among the cracked products, more propane and butanes were formed with small amounts of methane, ethane, pentanes, and hexanes. With increasing conversion, heptane isomers decreased, propane and butanes increased, and methane, ethane, pentanes, and hexanes also increased slowly. From these results, we conclude that the reaction proceeds successively according to the Reaction Scheme (A) by carbonium ion mechanism as follows:



REACTION SCHEME A

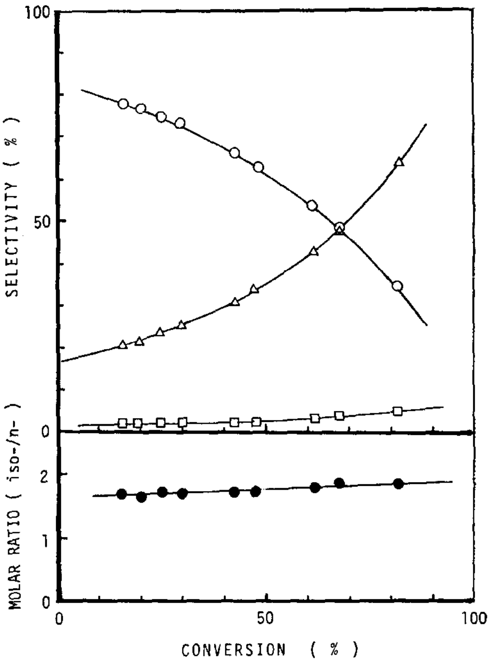


FIG. 2. Products distribution in hydrocracking of *n*-heptane as a function of conversion over tungsten oxide $WO_{3-\alpha}$ formed by reducing tungsten trioxide with hydrogen of 50 kg/cm² at 440°C over 100 hr. Reaction condition; 420°C, 50 kg/cm², and $H_2/n\text{-}C_7H_{16} = 8$. ○ isomerized C_7H_{16}, △ $C_3H_8 + C_4H_{10}$, □ $CH_4 + C_2H_6 + C_5H_{12} + C_6H_{14}$, ● C_4H_{10}.

The tungsten oxide, reduced below 445°C, with an active site for carbonium ion mechanism is named $WO_{3-\alpha}$. The values extrapolated to 0% conversion on the conversion reaction of *n*-heptane, obtained with similar experiments (Fig. 2) from 380 to 440°C, are shown in Table 1. With increasing reaction temperature, the selectivity of isomerized heptanes and the iso-/*n*- ratios of cracked products decreased

TABLE 1
EFFECT OF REACTION TEMPERATURE IN HYDROCRACKING OF n-HEPTANE OVER TUNGSTEN OXIDE WO_{3-a}

Reaction temperature (°C)	380	400	420	440
Selectivity (%)[a]				
$C_1 + C_2 + C_5 + C_6$	1	1	2	4
$C_3 + C_4$	6	10	16	30
isomerized C_7	93	89	82	66
k_2/k_1[b]	0.7	0.9	1.2	2.0
iso-/n- Ratio of C_4H_{10}	2.2	1.8	1.5	1.2
(Equilibrium values of C_4H_{10})[c]	0.81	0.76	0.71	0.66

[a] Values extrapolated to zero conversion.
[b] Values calculated for Reaction Scheme (A) at 70% conversion.
[c] From *7th World Petrol. Cong. Rev.* **4**, 135 (1968).

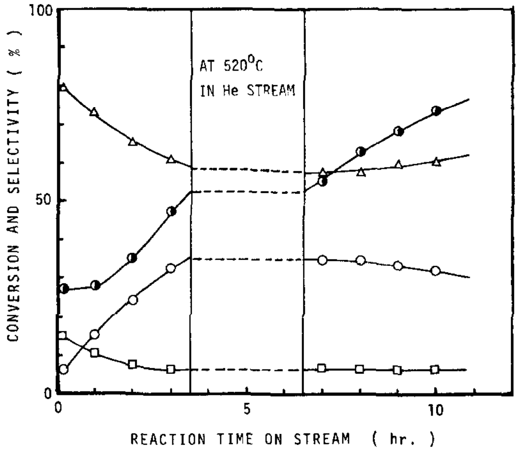


FIG. 3. Effect of thermal treatment under helium atmosphere in hydrocracking of n-heptane over tungsten trioxide at 442°C, LHSV = 5, H_2/n-C_7H_{16} = 8, and 50 kg/cm². ◑ conversion, ○ isomerized C_7H_{16}, △ $C_3H_8 + C_4H_{10}$, □ $CH_4 + C_2H_6 + C_5H_{12} + C_6H_{14}$.

and propane and butanes increased. These results suggest that the apparent activation energy of C–C bond breaking is larger than that of isomerization, because k_2/k_1 and k_3/k_1 increase with temperature. It was observed that the ratios of k_2/k_1 de-

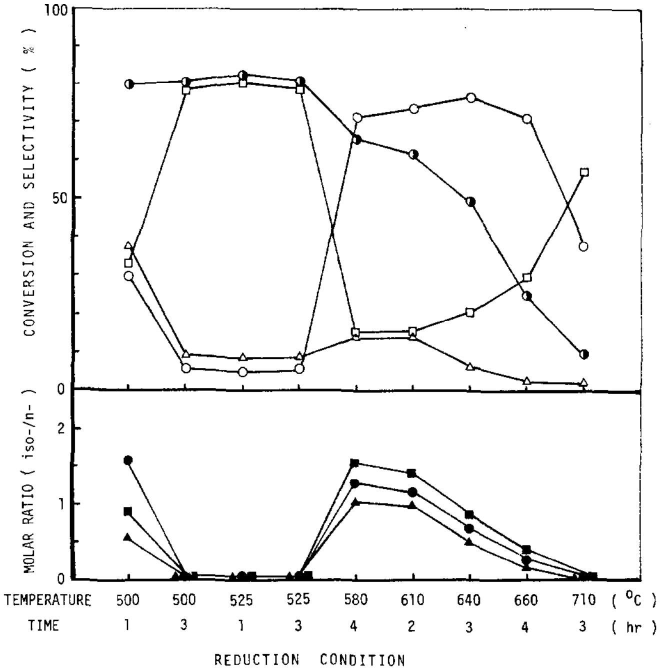


FIG. 4. Effect of reduction condition on the reaction products in hydrocracking of n-heptane over various tungsten oxides formed by continuously reducing tungsten oxide used in Fig. 1 with hydrogen of 50 kg/cm² at various temperatures. Reaction conditions; 440°C, LHSV = 5, H_2/n-C_7H_{16} = 8, and 50 kg/cm². ○ conversion, ○ isomerized C_7H_{16}, △ $C_3H_8 + C_4H_{10}$, □ $CH_4 + C_2H_6 + C_5H_{12}, + C_6H_{14}$, ● C_4H_{10}, ▲ $C\ H_{12}$, ■ C_6H_{14}.

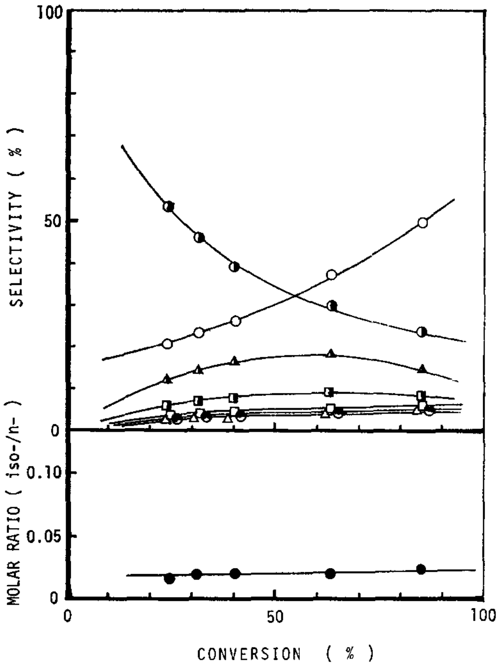
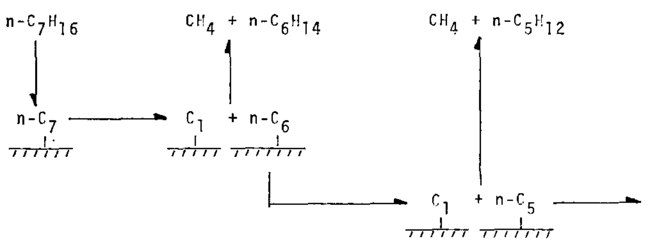


Fig. 5. Products distribution in hydrocracking of *n*-heptane as a function of conversion over tungsten oxide WO_{3-b} formed by reducing tungsten trioxide with hydrogen 50 kg/cm² at 520°C for 10 hr. Reaction conditions; 440°C, $H_2/n\text{-}C_7H_{16} = 8$, 50 kg/cm². ○ CH_4, △ C_2H_6, □ C_3H_8, ◨ (●) C_4H_{10}, ▲ C_5H_{12}, ◑ C_6H_{14}, ◓ isomerized C_7H_{16}.

creased slowly with the reaction time on stream. As shown in Fig. 3, the catalytic activity and the selectivity of hydrocracking of *n*-heptane with WO_{3-a} indicated a same tendency after a thermal treatment at 520°C in helium for 3 hr. Therefore, the increase in catalytic activity seems to arise only from the increase in the number of active sites on tungsten oxide by reduction with increasing reaction time on stream.

Figure 4 shows the effects of hydrogen reduction under pressure of 50 kg/cm² on activity and selectivity of tungsten oxide catalysts, obtained by continuous reduction of tungsten oxide WO_{3-a} used in Fig. 1. The total conversion showed approximately a constant value of about 80% over tungsten oxide reduced by hydrogen at 440°C (10 hr reaction, in Fig. 1) to 525°C for 3 hr, but the hydrocracking was always smaller. The decrease of reaction rate may have resulted from the decrease of active site due to sintering by hydrogen treatment at higher temperature. In the hydrocracking of *n*-heptane over tungsten oxide WO_{3-b} reduced at 500–525°C for 3 hr, only a little heptane was isomerized and more methane, ethane, pentanes, and hexanes were produced, with small amounts of the central cracking products. The ratios of iso-/*n*- in the hydrocracked products were small.

Figure 5 shows the results of hydrocracking of *n*-heptane with tungsten oxide WO_{3-b}, prepared by reduction of tungsten trioxide with hydrogen at 50 kg/cm² and 520°C for 10 hr. At low conversion major products were methane and *n*-hexane. Further increase in conversion resulted in the decrease of hexanes and increase of methane. At every conversion, the selectivity of isomerized heptanes and the values of iso-/*n*- ratio of hydrocracked products were very small. From these results, we may conclude that the conversion reaction of *n*-heptane over tungsten oxide WO_{3-b} proceeds by successive demethylation mechanism according to the Reaction Scheme (B).



Reaction Scheme B

This Reaction Scheme (B) of hydrocracking resembles hydrocracking with the metallic catalysts of nickel and cobalt. If the reaction proceeds by Reaction Scheme (B) of demethylation, isomerized products will not be produced. But small amounts of isomerized paraffins were produced as shown in Fig. 5. Separately we confirmed that the isomerization in the conversion reaction of *n*-heptane with tungsten oxide WO_{3-b} was due to trace amounts of oxygen and water contained in the feed of *n*-heptane; that is, the active site of demethylation mechanism was changed to that of carbonium ion mechanism by oxygen and water. This tungsten oxide WO_{3-b} was more unstable than any other tungsten oxides in air and it burned and oxidized quite rapidly to tungsten trioxide in the air even at room temperature.

As shown in Fig. 4, the products distribution of the hydrocracking of *n*-heptane over tungsten oxide WO_{3-c}, which was reduced by hydrogen of 50 kg/cm^2 at 580–610°C, has shown high selectivities for skeletally isomerized paraffins and centrally cracked products, and also high values of the iso-/*n*- ratios in hydrocracking products.

The results of the conversion reaction of *n*-heptane over tungsten oxide WO_{3-c}, obtained by reducing WO_3 by hydrogen of 50 kg/cm^2 at 590°C for 10 hr, are shown in Fig. 6. The selectivity of isomerized heptanes extrapolated to zero conversion was about 90%, that of propane plus butanes was about 10%, and others were negligibly small. The isomerized heptanes decreased proportionally with increasing conversion, and propane and butanes increased in equal moles. At every conversion, the values of iso-/*n*- ratio and central cracking were large. We conclude that the hydrocracking of *n*-heptane over tungsten oxide WO_{3-c} proceeds by carbonium ion mechanism. The conversion reaction over WO_{3-a} and WO_{3-c} proceeds by the same mechanism of carbonium ion, but the products distribution with these two tungsten oxides showed only a small difference. The ratios of iso-/*n*- of hydrocracking products and of k_2/k_1 of Reaction Scheme (A) with WO_{3-a} were larger than those with WO_{3-c}. These differences in conversion reaction may be caused by a stronger acidic character of WO_{3-a} or a very small amount of water produced by reduction of tungsten trioxide in WO_{3-a}.

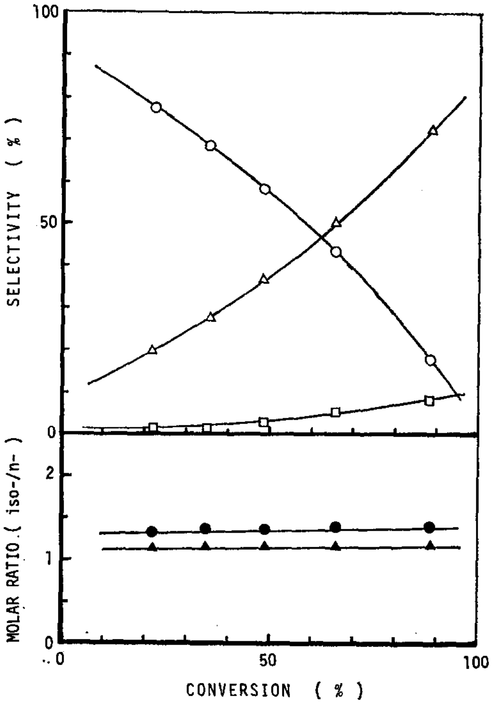


FIG. 6. Products distribution in hydrocracking of *n*-heptane as a function of conversion over tungsten oxide WO_{3-c} formed by reducing tungsten trioxide with hydrogen of 50 kg/cm^2 at 590°C for 10 hr. Reaction conditions; 440°C, $H_2/n\text{-}C_7H_{16} = 8$, and 50 kg/cm^2. ○ isomerized C_7H_{16}, △ $C_3H_8 + C_4H_{10}$, □ $CH_4 + C_2H_6 + C_5H_{12} + C_6H_{14}$, ● C_4H_{10}, ▲ C_5H_{12}.

Previously we have shown that a conversion reaction of $C_4 \sim C_8$ paraffinic hydrocarbons with a tungsten oxide–alumina catalyst, which was reduced by hydrogen of 50 kg/cm^2 at 670°C for 10 hr, proceeded by carbonium ion mechanism (*21*). The previous tungsten oxide on alumina should be in the same oxidation state as WO_{3-c} because X-ray diffraction pattern and the kind of reaction products were consistent. These results indicate that the tungsten trioxide supported on alumina is more stabilized against hydrogen reduction than unsupported tungsten trioxide. The tungsten trioxide supported on silica was not more stable than unsupported tungsten trioxide.

The conversion reaction of *n*-heptane

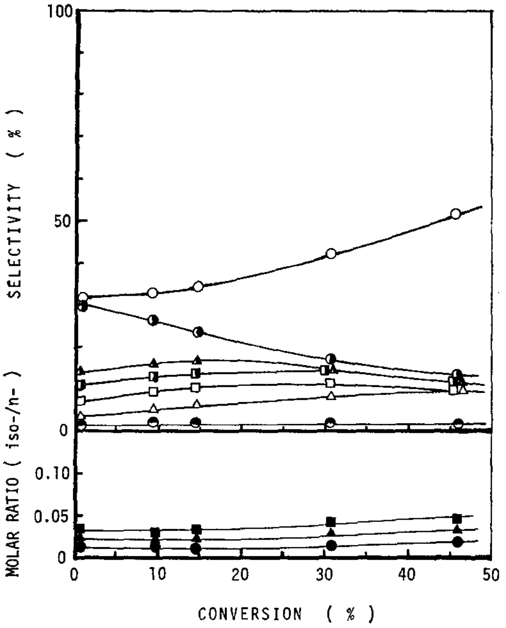


FIG. 7. Products distribution in hydrocracking of *n*-heptane as a function of conversion over tungsten metal powder at 500°C, $H_2/n\text{-}C_7H_{16} = 8$, and 50 kg/cm². ○ CH_4, △ C_2H_6, □ C_3H_8, ◨ (●) C_4H_{10}, ◭ (▲) C_5H_{12}, ◑ (■) C_6H_{14}, ◓ isomerized C_7H_{16}.

with tungsten oxide WO_{3-d}, reduced by hydrogen of 50 kg/cm² at 710°C, had shown a very low conversion, showing a slow change in the reaction mechanism. The selectivities for isomerized heptanes, propane plus butanes and the ratios of iso-/*n*- of hydrocracked products decreased and the selectivities for methane, ethane, pentanes, and hexanes increased clearly during the course of reaction. These results suggest that the active site changed gradually from the Reaction Scheme (A) to the Reaction Scheme (B). As discussed later, the composition of tungsten oxide WO_{3-d} reduced at 710°C was established as metallic tungsten by X-ray analysis and thermobalance. The hydrocracking of *n*-heptane with commercial pure tungsten metal is shown in Fig. 7. The products indicate that the conversion reaction proceeds almost exclusively by the Reaction Scheme (B) of demethylation mechanism like WO_{3-b}, metallic nickel and cobalt. The intermediate products with tungsten metal and WO_{3-d}, where the conversion reaction proceeds by the Reaction Scheme (B), were smaller than those with WO_{3-b}. This result should suggest that the hydrocarbons were adsorbed stronger on tungsten metal and WO_{3-d} than on WO_{3-b}, and that the adsorbed hydrocarbons were hydrocracked successively without desorption. Anderson (*3*) reported that isomerized butane was produced in 12% yield on the conversion reaction of *n*-butane with evaporated tungsten film. As shown in Fig. 7 of this paper, isomerized heptanes are produced in 2% yield in the conversion reaction of *n*-heptane with tungsten metal powder. The impurity in catalyst may be a more important factor for this difference than a nature of hydrocarbons, reaction conditions and others.

These results strongly suggest that the catalysis of tungsten oxide on the conversion reaction of *n*-heptane changes at least four times by hydrogen reduction at various temperatures. The catalysts of every oxidation state, that is, WO_{3-a}, WO_{3-b}, WO_{3-c}, and WO_{3-d}, were easily oxidized to tungsten trioxide of yellowish crystalline at comparatively lower temperature in air and the tungsten trioxides reoxidized has shown the same type catalysis on the conversion reaction in the course of reduction. The tungsten trioxides reproduced under mild condition were easily reduced to lower oxidation state of tungsten because of insufficient crystallization; that tungsten trioxide was reduced the same cycle.

X-Ray Analysis of Various Kinds of Reduced Tungsten Oxide

Tungsten oxide, produced by the calcination of ammonium paratungstate at 550°C for 10 hr in air stream, was a yellowish crystalline and has shown quite a sharp X-ray diffraction pattern consistent with the standard pattern of tungsten trioxide (*22*) (see Fig. 8). After the reduction of the tungsten trioxide by hydrogen of 50 kg/cm² at 445°C for 10 hr, the blue crystalline was obtained and regarded to be tungsten oxide WO_{3-a} from its catalysis in the conversion reaction of *n*-heptane. The X-ray diffraction pattern of this crystalline was broad and weak probably because

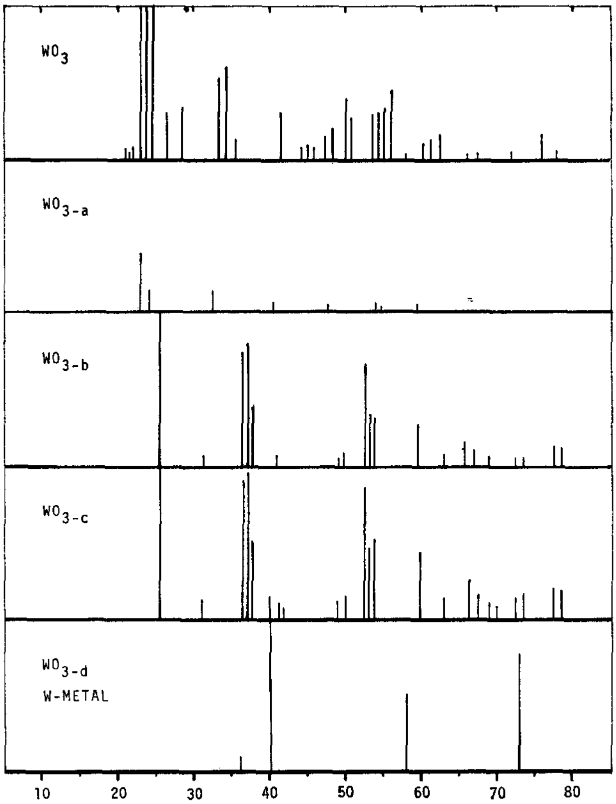


FIG. 8. X-ray diffraction pattern of various tungsten oxides. Reduction condition of tungsten trioxide; WO_{3-a} at 445°C, WO_{3-b} at 520°C, WO_{3-c} at 590°C, and WO_{3-d} at 720°C with hydrogen of 50 kg/cm² for 10 hr.

of disordered structure, and coincided well with that of standard $WO_{2.9}$ (*22*). Tungsten oxide, which was reduced by hydrogen of 50 kg/cm² at 440°C over 100 hr, has shown the same X-ray diffraction pattern, color, and catalysis of tungsten oxide WO_{3-a}.

When tungsten trioxide was reduced at 520°C with hydrogen of 50 kg/cm² for 10 hr, brown crystalline was obtained. This tungsten oxide was regarded as WO_{3-b} according to conversion reaction of *n*-heptane, and its sharp and strong X-ray diffraction pattern has shown a complete agreement with that of standard tungsten dioxide (*22*), indicating grown-up crystalline. The X-ray analysis of this tungsten oxide was carried out after adsorbing *n*-heptane including 0.1% liquid paraffin at room temperature in order to cover the surface and prevent rapid oxidation of this tungsten oxide.

Brown tungsten oxide, obtained by the reduction of tungsten trioxide at 590°C with hydrogen of 50 kg/cm² for 10 hr, displayed the catalysis due to tungsten oxide WO_{3-c} and presented an X-ray diffraction pattern which completely coincided with that of standard tungsten dioxide.

Gray tungsten oxide, formed by the reduction of tungsten trioxide at 720°C with hydrogen of 50 kg/cm² for 10 hr and regarded as tungsten oxide WO_{3-d} according to conversion reaction of *n*-heptane, showed an X-ray diffraction pattern quite similar to that of standard tungsten metal and commercial pure tungsten metal.

Thermobalance Study on the Reduction of Tungsten Oxide

The decrease in weight of tungsten oxide under hydrogen atmosphere was measured by a thermobalance with the heating rate of 1°C/min. At least two stable oxidation

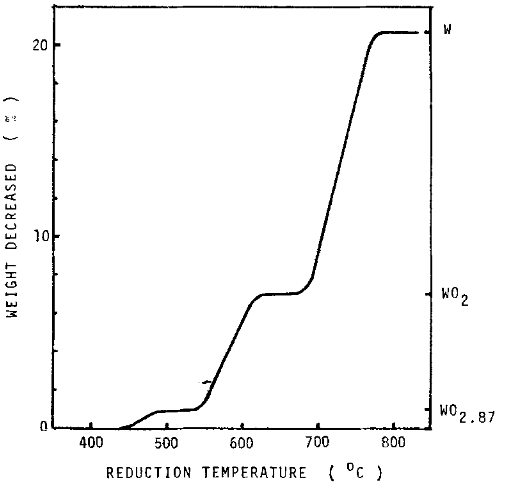


FIG. 9. Weight decrease of tungsten trioxide under hydrogen stream as a function of temperature with heating rate 1°C/min.

states of tungsten oxide for hydrogen reduction were found to exist from tungsten trioxide to tungsten metal as shown in Fig. 9.

The decrease in weight of tungsten trioxide under hydrogen atmosphere at 440°C, 460°C, and 480°C is shown in Fig. 10. Tungsten trioxide could be reduced to $WO_{2.84}$ at 440°C after about 40 hr, and this crystalline $WO_{2.84}$ was quite stable even after 73 hr at 440°C. The X-ray diffraction pattern of this tungsten oxide $WO_{2.84}$ has shown a complete agreement with that of standard $WO_{2.9}$ and this $WO_{2.84}$ was regarded to be WO_{3-a} according to the conversion reaction of *n*-heptane. Tungsten oxide WO_{3-a}, which was reduced by hydrogen of 50 kg/cm^2 at 445°C for 10 hr and at 440°C over 100 hr, has the same X-ray diffraction pattern of $WO_{2.9}$, blue crystalline and an active site of carbonium ion mechanism. In view of these facts, the tungsten trioxide was not reduced over $WO_{2.84}$ below 440°C. The structure of $WO_{2.9}$ is proposed to have the shear structure, in which one oxygen layer is slipped out per twenty layers of $(3\bar{1}0)$ of tungsten trioxide and a distance of the shear plane is about 25 Å. If the tungsten oxide $WO_{2.84}$ was produced by the same mechanism from tungsten trioxide, the structure of $WO_{2.84}$ should be composed of shear structure, in which one oxygen layer is slipped out per thirteen planes of $(3\bar{1}0)$ of tungsten trioxide and a distance of shear plane may be about 16 Å. This assumption is supported by the broad and weak X-ray diffraction pattern of WO_{3-a}. After the reduction of $WO_{2.84}$ at 525°C under hydrogen atmosphere for one hour, the tungsten oxide was reduced to tungsten oxide of lower oxidation state even at 440°C. This might be due to the destruction of the comparatively stabilized struc-

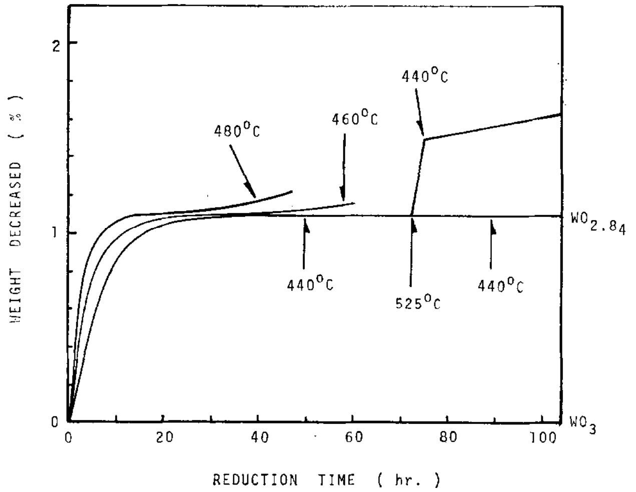


FIG. 10. Weight decrease of tungsten trioxide under hydrogen stream as a function of reduction time at various temperatures.

ture of $WO_{2.84}$ crystalline and the comparatively weak W–O bond energy of the shear structure of $WO_{2.84}$. The reduction rate of WO_3 to $WO_{2.84}$ were almost constant in a wide range of reduction degrees. It seems than an oxygen atom with the same W–O bond energy in the same structure and the same situation has been reduced. The active site of the conversion reaction over $WO_{2.84}$ should be oxygen vacancy of tungsten trioxide, since the conversion reaction of *n*-heptane with tungsten trioxide having the active site for carbonium ion mechanism increased with reaction time on stream (Fig. 1), and tungsten trioxide was reduced only to $WO_{2.84}$ at 440°C (Fig. 10). Thus, the active site of WO_{3-a} is the oxygen vacancy of tungsten trioxide structure and the value of a of WO_{3-a} is about 0.16. The climb of a dislocation through the lattice of oxygen vacancy in tungsten trioxide [which was also pointed out by Anderson (*23*)] may have a small effect on the activity of catalyst because (a) the increase of active site results from the reduction of tungsten trioxide and can not well involve the effect of thermal treatment in helium (Fig. 3) and (b) the active site is indeed increased (but very slowly) during the reaction after 100-hr reduction by hydrogen of 50 kg/cm^2 at 440°C, where tungsten trioxide is reduced sufficiently to $WO_{2.84}$ as shown in Fig. 10.

The results of reduction of tungsten trioxide over 520–575°C are shown in Fig. 11. The rates of reduction increased with increasing reduction temperature. The tungsten trioxide was reduced to tungsten dioxide in hydrogen atmosphere at 520°C in about 55 hr, but no further reduction occurred even over 100 hr. Since an active site of demethylation mechanism of the tungsten oxide WO_{3-b} in the conversion reaction of *n*-heptane was brought by the reduction at temperatures 500–525°C, the composition of the tungsten oxide WO_{3-b} seems to be nearly tungsten dioxide and may be tungsten dioxide or tungsten oxide $WO_{2+\alpha}$, where α represents a very small value not measurable by thermobalance. Because tungsten dioxide is very stable with respect to hydrogen reduction under 525°C, the tungsten oxide WO_{3-b} is tungsten dioxide as indicated from X-ray diffraction pattern analysis. Both of the two active sites, carbonium ion type and demethylation type, existed on tungsten oxide reduced at 500°C after one hour as shown in Fig. 3. Since the reduction rates of $WO_{2.84}$ to tungsten dioxide were constant in a wide range of reduction degrees, it may be suggested that the oxygen atom of the same W–O bond energy and the same situation in the structure has been reduced. Although tungsten dioxide was reduced to WO_{2-x} at 660°C, it was not further reduced

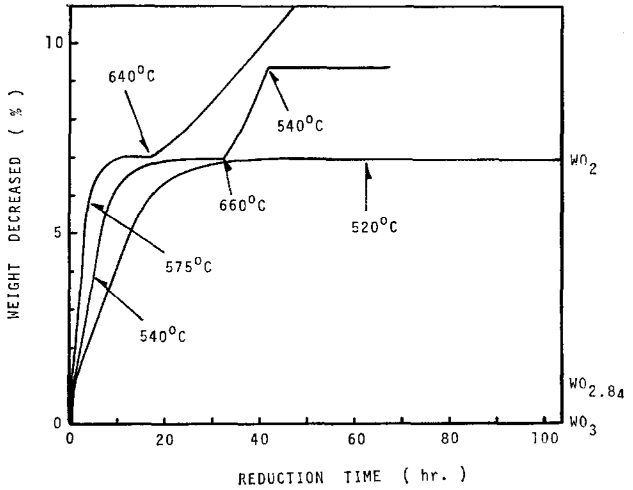


FIG. 11. Weight decrease of tungsten trioxide under hydrogen stream as a function of reduction time at various temperatures.

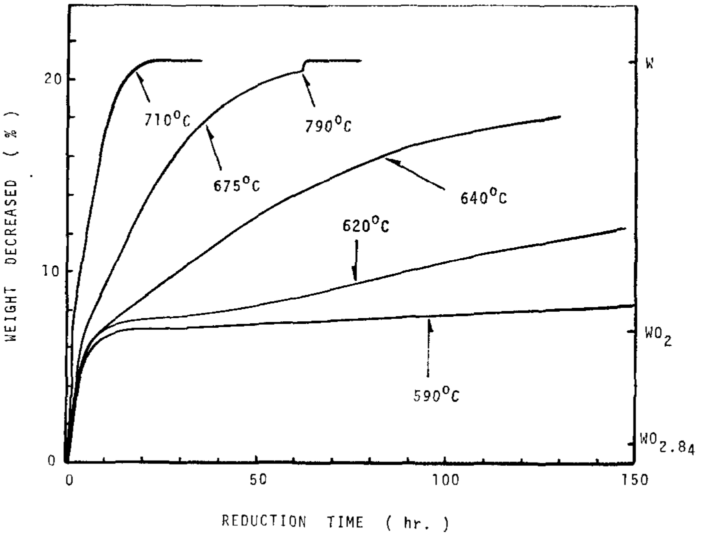


FIG. 12. Weight decrease of tungsten trioxide under hydrogen stream as a function of reduction time at various temperatures.

at 540°C. This indicates that the W–O bond of tungsten dioxide is stronger than that of $WO_{2.84}$.

As shown in Fig. 4, tungsten oxide WO_{3-c}, reduced at temperature from 580°C to 610°C, has shown a catalytic activity of carbonium ion mechanism for the conversion reaction of *n*-heptane, and its X-ray diffraction pattern coincided with that of tungsten dioxide. The reduction rate of tungsten trioxide over tungsten dioxide in the hydrogen atmosphere was slow at 590–620°C as shown in Fig. 12, tungsten trioxide could not be reduced to tungsten metal in 100 hr, and X-ray diffraction pattern of tungsten dioxide had indicated tungsten oxide $WO_{2-\beta}$, where β was a small value. Therefore, tungsten oxide WO_{3-c} is $WO_{2-\beta}$.

The results of conversion reaction of *n*-heptane, X-ray analyses and the thermobalance analyses obviously suggest that the active site of tungsten oxide for carbonium ion type conversion reaction should be oxygen vacancy of stable structures of tungsten trioxide and tungsten dioxide.

Tungsten trioxide was reduced easily to tungsten metal at 710°C as shown in Fig. 12. Tungsten oxide WO_{3-d} reduced by hydrogen of 50 kg/cm^2 at 710°C has shown an activity of demethylation type for conversion reaction of *n*-heptane and a diffraction pattern of the tungsten metal by X-ray analysis. The active site of commercial tungsten metal was of demethylation type. Then tungsten oxide WO_{3-d} should be tungsten metal or tungsten oxide WO_{α} where α represents a very small value.

The results obviously indicate that the active site of demethylation type reaction of *n*-heptane is electronic stable structures of tungsten dioxide and tungsten metal, or tungsten oxide with very little oxygen, that is, $WO_{2+\alpha}$ and WO_{α} where α is zero or a very small value.

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