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Hydrocracking of Tetralin on Supported Nickel-Tungsten Catalysts

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The hydrocracking of tetralin was carried out over supported nickel–tungsten (NiO 3%, WO_3 20%) on silica–alumina, alumina, and silica catalysts at a hydrogen pressure of 100 atm and in the temperature range from 325 to 375 °C. The total conversion of tetralin and the product composition of hydrocracking were measured for the catalysts. The influence of pretreatment of the catalysts with H_2 and H_2S on the conversion and product composition was investigated for each catalyst. The hydrocracking of decalin was also carried out under the same conditions. It is found that the hydrocracking of tetralin proceeds along two reaction paths: (A) hydrogenation to decalin followed by conversion to methylperhydroindenes and C_{10}-naphthenes, (B) isomerization to methylindans followed by cracking to butylbenzene. The selectivity of each reaction path and the catalytic properties are discussed.

Catalytic hydrocracking is of considerable importance in petroleum refining. In the course of the commercial growth of the petroleum industry, the chemistry of hydrocracking over various catalysts has been studied with pure hydrocarbons. Most hydrocracking catalysts of commercial interest are of dual nature, consisting of both a hydrogenation–dehydrogenation component and an acidic support.

Recently, the chemistry of hydrocracking of typically pure hydrocarbons has been reviewed by Langlois and Sullivan,[1] and the mechanism for hydrocracking of polynuclear aromatic hydrocarbons on silica–alumina based dual-functional catalysts (CoS, MoS_2, NiS, WS_2, *etc.*) has been investigated by Qader.[2] Hydrocracking is found to proceed through sequential hydrogenation, isomerization and cracking reactions. Also, the reaction is found to follow first-order kinetics and the data are found compatible with the dual-site mechanism of Langmuir-Hinshellwood.

Sullivan *et al.*[3] have found considerable cyclization of the side chain when certain aromatic hydrocarbons (phenanthrene, anthracene, pyrene, *etc.*) are hydrocracked over a nickel sulfide on silica–alumina catalyst. The product is found to be predominantly tetrahydronaphthalene (tetralin) of lower moleculer weight than that of the reactant.

In this paper, the hydrocracking of tetralin was carried out as a test reaction to clarify the selectivity of hydrocracking catalysts. Supported nickel–tungsten on silica–alumina, alumina and silica catalysts were used. Effect of the carrier in the supported catalysts on the selectivity of hydrocracking was observed to significant extent. Also, the product composition changed extensively with catalyst pretreatment. On sulfiding the silica–alumina supported catalyst with H_2S, the principal reaction was found to be the hydrogenation to perhydronaphthalene (decalin), which was further converted to methylperhydroindenes and C_{10}-naphthenes. While for the catalysts pretreated with H_2, isomerization to methylindans and cracking to butylbenzene occurred predominantly.

The selectivity of each reaction path seems to depend on the relative strength of the acidic and hydrogenation components on the catalysts.

Experimental

Equipment. The experiments were performed in a continuous flow system with a fixed bed reactor, a flow diagram of which is shown in Fig. 1. The catalyst (16—32 mesh, 5 ml) was supported inside a 12 mm i.d. by 680-mm long stainless-steel tube which was surrounded by an electric furnace. The catalyst temperature was measured by a chromel–alumel thermocouple located in a thermowell in the catalyst bed.

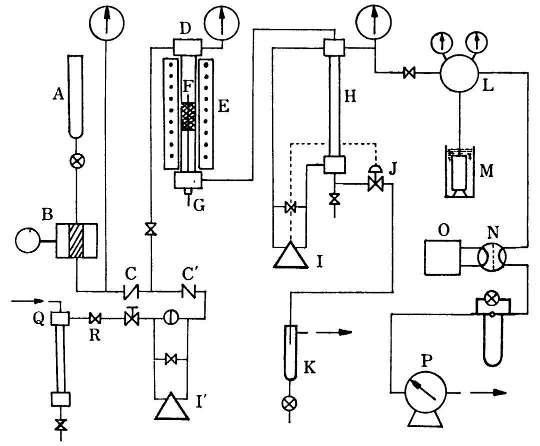

Fig. 1. Reaction apparatus.
A: Reactant vessel, B: plunger pump, C,C′: non return valve, D: reactor, E: furnace, F: catalyst bed, G: thermocouple, H: separator, I,I′: D.P. cell, J: level control valve, K: reservoir, L: pressure control valve, M: standard pressure vessel, N; six way valve, O: gas chromatograph, P: gas meter, Q: gas purifier, R: flow control valve.

Tetralin or decalin was fed by a plunger pump, and purified hydrogen was fed through a needle valve. The effluent from the reactor was taken to a gas-liquid separator. The liquid from the separator was automatically effluent by a revel control valve. The gas, passing through a six-way valve, was measured with a gas meter. Both the gas and liquid were analyzed by a gas chromatograph.

The reaction was carried out in the temperature range from 325 to 375 °C at a pressure of 100 atm. The liquid hourly space velocity (LHSV) was 8 per h and the molar ratio of hydrogen to the hydrocarbon was 10. In order to collect products representative of steady-state reaction conditions, the first hour was taken as off-stream time for bringing the reaction system to a steady state.

Analysis. The products were analyzed with a Hitachi Model K-53 gas chromatograph with flame-ionization detectors and with a squalan capillary column (90 m×0.25 mm) at 90 °C. In the identification of each product on the chromatogram, the information[4,5] from the capillary gas chromatographic method for determining the C_3–C_{12} hydrocarbons in full-range moter gasolins was applied.

The peak areas in the chromatograms were measured with a Hewlett-Packerd Model 3380A reporting integrator.

Catalysts and Chemicals. The catalysts consisted of supported nickel-tungsten (3% NiO, 20% WO_3) on commercial alumina (Ketjenfine pure alumina), silica–alumina (25% Al_2O_3, Nikki Kagaku N 633H) and silica carriers. These catalysts were prepared by impregnating the carriers with a solution of nickel nitrate and ammonium paratungstate. The impregnated materials were oven-dried and calcined in air at 500 °C for 10 h.

Prior to reaction, they were reduced in flowing hydrogen at 500 °C for 16 h. In some experiments, they were sulfided with 10% H_2S in H_2 after the reduction.

Surface areas, determined by the standard BET method, were 226 m^2/g for the silica–alumina supported catalyst, 186 m^2/g for the alumina-supported catalyst, 156 m^2/g for the silica-supported catalyst.

Tetralin and decalin were commercial extra-pure reagents (Kokusan Kagaku, 99% purity) and were used without further purification. The decalin consisted of 54% *trans*-decalin and 45% *cis*-decalin.

Results and Discussion

Product Composition and Reaction Path. The total conversions of tetralin and the product compositions for hydrocracking on a nickel–tungsten–silica–alumina catalyst pretreated with H_2S are shown in Table 1. At a temperature of 325 °C, the main product is decalin, and the other products are divided into methylindans, methylperhydroindenes, C_{10}-naphthenes, C_6-compounds,[6] butylbenzene, and naphthalene. The selectivities of each product (the ratio of the yield to the total conversion) were calculated from this table and are shown in Fig. 2. At higher temperatures,[7] the selectivity for decalin and methylperhydroindenes decreased, whereas both the yields and selectivities of other products increased.

TABLE 1. HYDROCRACKING OF TETRALIN ON A SULFIDED NICKEL–TUNGSTEN–SILICA–ALUMINA CATALYST

Hydrogen pressure, 100 atm; LHSV, 8; H_2/Tetralin, 10.

Temperature °C	325	350	375
Total conversion mol %	9.8	13.2	22.6
Product composition mol/100 mol charge			
C_6-Compounds	0.2	0.8	2.2
C_{10}-Naphthenes	0.8	1.9	7.3
Methylperhydroindenes	2.2	2.4	3.4
Butylbenzene	0.6	0.9	1.7
Methylindans	0.3	0.7	1.7
Decalin	4.4	5.2	4.5
Tetralin	90.2	87.4	77.4
Naphthalene	0.8	1.3	1.5

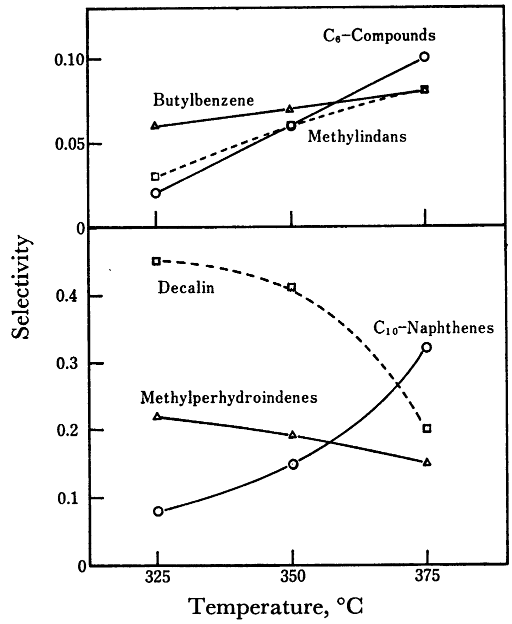

Fig. 2. Selectivity for hydrocracking of tetralin.

TABLE 2. HYDROCRACKING OF DECALIN ON A SULFIDED NICKEL–TUNGSTEN–SILICA–ALUMINA CATALYST

Hydrogen pressure, 100 atm; LHSV, 8; H_2/Decalin, 10.

Temperature °C	325	350	375
Total conversion mol %	6.3	18.2	33.5
Product composition mol/100 mol charge			
C_{10}-Naphthenes	2.6	10.8	22.5
Methylperhydroindenes	3.7	7.4	11.0
Decalin	93.7	81.2	66.5

In Table 2, the conversions and the product compositions for the hydrocracking of decalin are shown under the same conditions and catalyst as for the tetralin reaction (in Table 1). The principal products are methylperhydroindenes and C_{10}-naphthenes.

From a comparison of the above product compositions for the hydrocracking of tetralin and decalin, it is suggested that hydrogenation to decalin occurred predominantly in the first step during the reaction at a lower temperature and then the isomerization of decalin to methylperhydroindenes occurred in the second step. Then the methylperhydroindenes were further converted to C_{10}-naphthenes in the third step. At higher temperatures, the isomerization to methylindans and cracking to butylbenzene also occurred to a significant extent.

These data indicate that the hydrocracking of tetralin is divided into two types of reaction paths as shown in

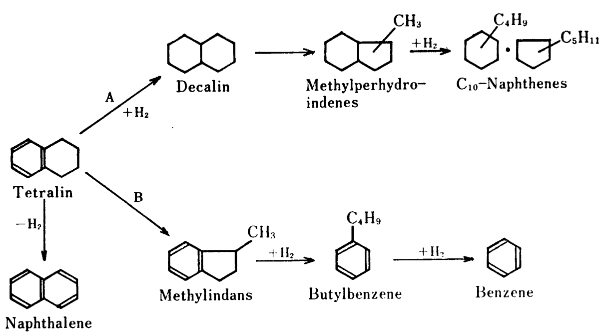

Fig. 3. Mechanism of hydrocracking of tetralin.

TABLE 3. HYDROCRACKING OF TETRALIN ON SUPPORTED NICKEL–TUNGSTEN CATALYSTS
Hydrogen pressure, 100 atm; Temperature, 350 °C; LHSV, 8; H_2/Tetralin, 10.

Catalysts	Nickel–Tungsten–Silica–Alumina		Nickel–Tungsten–Alumina		Nickel–Tungsten–Silica		Silica–Alumina
Pretreatment	H_2S	H_2	H_2S	H_2	H_2S	H_2	H_2
Total conversion mol %	13.2	7.6	35.4	17.5	24.0	0.4	4.0
Product composition mol/100 mol charge							
C_6-Compounds	0.8	2.0	—	1.2	—	—	—
C_{10}-Naphthenes	1.9	0.5	0.9	3.2	—	—	—
Methylperhydroindenes	2.4	0.5	—	2.5	—	—	—
Butylbenzene	0.9	0.7	—	2.6	—	—	0.6
Methylindans	0.7	1.2	—	1.9	—	—	1.7
Decalin	5.2	1.7	34.2	5.3	23.8	0.2	—
Tetralin	87.4	92.4	64.6	82.1	76.0	99.6	96.0
Naphthalene	1.3	1.1	0.3	0.8	0.2	0.2	1.8

Fig. 3: (A) hydrogenation to decalin followed by conversion to methylperhydroindenes and C_{10}-naphthenes, and (B) isomerization to methylindans and cracking to butylbenzene followed by conversion to benzene.

Effect of Pretreatment and Carriers of Catalysts. In the hydrocracking of tetralin, the influence of pretreatment of the supported nickel–tungsten catalysts with H_2 and H_2S on the product composition was investigated. In Table 3, the conversions of tetralin and the product compositions on three supported catalysts, silica–alumina-, alumina-, and silica-supported catalysts, were measured at 350 °C. The conversion of tetralin and the product composition for each sulfided catalyst were quite different from those of the reduced catalyst. The conversion on the reduced catalyst was lower than that on the sulfided catalyst in each case.

The decalin yield on the silica–alumina supported catalyst treated with H_2S was higher than that on the reduced catalyst, and the yield of methylperhydroindenes and C_{10}-naphthenes were also higher. However, the yield of methylindans and C_6-compounds on the reduced catalyst were higher than those on the sulfided catalyst.

In the hydrocracking of decalin, the influence of the pretreatment of these catalysts on the decalin conversion was investigated. In Table 4, the conversions on the silica–alumina- and alumina-supported catalysts treated with H_2 and H_2S are compared. The conversion on the silica–alumina-supported catalyst treated with H_2 was about seven times that on the catalyst treated with H_2S. On the alumina-supported catalyst, the reaction was extensively inhibited by the sulfidation. The conversion for the silica–alumina catalyst alone was comparable to that on the sulfided silica–alumina-supported catalyst.

TABLE 4. HYDROCRACKING OF DECALIN ON SUPPORTED NICKEL–TUNGSTEN CATALYSTS
Hydrogen pressure, 100 atm, Temperature, 350 °C, LHSV, 8, H_2/Decalin, 10.

Catalysts	Nickel–Tungsten–Silica–Alumina		Nickel–Tungsten–Alumina		Silica–Alumina
Pretreatment	H_2S	H_2	H_2S	H_2	H_2
Total conversion mol %	6.3	42.4	—	36.2	7.0
Product composition mol/100 mol charge					
C_{10}-Naphthenes	2.6	29.0	No reaction	23.8	2.0
Methyl-perhydroindenes	3.7	13.2		12.3	5.0
Decalin	93.7	57.6		63.8	93.0

From the above observation for hydrocracking on these catalysts, the selectivity of catalysts is discussed in relation to several recent reports.

Selectivity of Hydrocracking Catalysts. Some data have been reported on tetralin hydrocracking over nickel sulfide on silica–alumina catalysts.

Flinn *et al.*[8] have reported that ring opening and hydrogenation are the predominant reactions at 68 atm and 412 °C, and light alkanes are produced with a high ratio of branched to unbranched alkanes.

Sullivan *et al.*[3] have reported that the fused bicyclic cycloalkanes as main products are produced by the hydrocracking of tetralin at 288 °C and 82 atm.

However, the reaction path of the hydrocracking was not discussed in these reports.

TABLE 5. SELECTIVITY FOR HYDROCRACKING OF TETRALIN ON SUPPORTED NICKEL–TUNGSTEN CATALYSTS

Catalysts	Nickel–Tungsten–Silica–Alumina		Nickel–Tungsten–Alumina		Nickel–Tungsten–Silica
Pretreatment	H_2S	H_2	H_2S	H_2	H_2S
Total conversion mol %	13.2	7.6	35.4	17.5	24.0
Selectivity					
Path A	*0.74*	*0.36*	*0.98*	*0.64*	*0.99*
C_{10}-Naphthenes	0.15	0.07	0.02	0.18	—
Methyl-perhydroindenes	0.19	0.07	—	0.15	—
Decalin	0.40	0.22	0.96	0.31	0.99
Path B	*0.17*	*0.50*	—	*0.31*	—
C_6-Compounds	0.06	0.26	—	0.06	—
Methylindans	0.05	0.15	—	0.10	—
Butylbenzene	0.06	0.09	—	0.15	—
Naphthalene	*0.09*	*0.14*	*0.02*	*0.05*	*0.01*

In the present paper, it was demonstrated that the hydrocracking of tetralin proceeds along two reaction paths (A and B) as shown in Fig. 3. According to the mechanisms, the selectivity calculated from the product composition in Table 3 are shown in Table 5. The selectivity for all naphthenes produced for path A was 0.74 on the sulfided silica–alumina supported catalyst, whereas it was 0.36 on the reduced catalyst. On the alumina-supported catalyst treated with H_2S and H_2, the selectivities were 0.98 and 0.64, respectively. The selectivity for the sulfided silica-supported catalyst was 0.99.

The total conversion of tetralin on each catalyst treated with H_2S was generally higher than that on the reduced catalyst. As shown in Table 4, the activity of the sulfided catalyst for decalin hydrocracking was lower than that of the reduced catalyst.

It is suggested from the above observations that the active sites for hydrogenation of tetralin on the catalyst are produced by means of sulfidation, while the acid sites producing isomerization and the cracking of tetralin and decalin are decreased upon sulfidation.

Langlois *et al.*[9] have found that, with sulfiding a nickel on silica–alumina catalyst, the total conversion of decane hydrocracking greatly increased and the predominant reaction changed from isomerization to cracking. They postulated that the catalyst before sulfidation contained both nickel metal and nickel salts at the silica–alumina acid site, and upon sulfidation the nickel metal was converted to nickel sulfide, and the H_2S reacted with the nickel–silica–alumina salt to regenerate the original strong acid sites of the silica–alumina support.

In this paper, it is suggested that on the silica–alumina supported catalyst treated with H_2S, the original acid sites of the silica–alumina carrier are effective for the isomerization and cracking of tetralin. Also, by reducing the catalyst, acidic sites are formed on the surface of the supported tungsten oxide. Upon sulfidation of the alumina supported catalyst, no hydrocracking of decalin occurs. However, the hydrocracking activity of the reduced catalyst is higher. Therefore, the acidic properties of the catalyst are assumed to be formed by reduction with H_2.

The sulfidation of tungsten oxide supported on silica–alumina catalysts has been studied by Massoth and Bidlack.[10] Supported catalysts and bulk WO_3 were sulfided with mixture of H_2S and H_2 at temperatures between 260 and 594 °C and at a H_2S partial pressure of 0.1—5 atm. Studies of partially reacted samples show the sulfided species to be WS_2 and the unconverted oxide to be $W_{20}O_{58}$, suggesting that partial reduction precedes sulfidation. The salient findings of their study are: (1) reduction of bulk WO_3 by H_2 proceeds rapidly to $W_{20}O_{58}$ and then more slowly to W metal, (2) the sulfidation of bulk WO_3 by H_2S–H_2 mixtures proceeds rapidly through the formation of $W_{20}O_{58}$, followed by a slower reaction to WS_2, and (3) the mechanisms of sulfidation for bulk and supported WO_3 are similar.

The catalytic structure of nickel–tungsten sulfide as a hydrogenation catalyst has been investigated by Voorhoeve[11] using the ESR technique. It was concluded that the active sites for benzene hydrogenation in a wide variety of tungsten–disulfide based catalysts are tungsten ions, probably in the trivalent state. Nickel appears to have an indirect influence on the hydrogenation activity in Ni–W–S rather than acting as the active center.

It is apparent that the state of tungsten on the sulfided catalyst surface in the present study is probably attributable to WS_2. According to the above conclusions reported by Voorhoeve,[11] it is apparent that the active sites for the hydrogenation of tetralin are the tungsten ions of tungsten disulfide crystals on the catalyst.

On the reduced alumina-supported catalyst, the acidic catalyzed isomerization and cracking activity is attributed to the acidic hydroxyl groups over the partially-reduced surface of tungsten oxide supported on alumina.

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References

1) G. E. Langlois and R. F. Sullivan, "Advances in Chemistry Series No. 97, Refining Petroleum for Chemicals," ACS (1970), Chap. 3, p. 38.
2) S. A. Qader, *J. Inst. Petroleum*, **59**, 178 (1973).
3) R. F. Sullivan, C. J. Egan, and G. E. Langlois, *J. Catal.*, **3**, 183 (1964).
4) W. N. Sanders and J. B. Maynard, *Anal. Chem.*, **40**, 527 (1968).
5) P. Merchant, *Anal. Chem.*, **40**, 2153 (1968).
6) Contains 90% benzene.
7) Only small amounts of butane were observed at 375 °C.
8) R. A. Flinn, O. A. Larson, and H. Beuther, *Ind. Eng. Chem.*, **52**, 153 (1963).
9) G. E. Langlois, R. F. Sullivan, and C. J. Egan, *J. Phys. Chem.*, **70**, 3666 (1966).
10) F. E. Massoth and D. L. Bidlack, *J. Catal.*, **16**, 303 (1970).
11) R. J. H. Voorhoeve, *J. Catal.*, **23**, 236 (1971).