Journal of Catalysis **186,** 45–56 (1999)
Article ID jcat.1999.2546, available online at http://www.idealibrary.com on IDEAL®

Hydrocracking of Tetralin over NiW/USY Zeolite Catalysts: For the Improvement of Heavy-Oil Upgrading Catalysts

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Received November 9, 1998; revised April 26, 1999; accepted May 4, 1999

The reaction mechanisms of tetralin as a model compound of heavy petroleum fractions were investigated with the aim of improving bifunctional USY zeolite-based catalysts for heavy-oil hydrocracking. The major reaction path in the initial period was found to differ from that later in the reaction. In the initial reaction period, over USY catalysts with and without NiW sulfide, the reaction began with the formation of phenylbutyltetralin from two tetralin molecules by electrophilic aromatic substitution. Phenylbutyltetralin subsequently decomposed into benzene and octahydro tricyclic aromatic compounds. These reactions were catalyzed without the involvement of gaseous hydrogen and very likely lead to coke formation by chain reactions. Later in the reaction, tetralin and the above-mentioned heavy compounds were gradually hydrocracked over the bifunctional USY-supported NiW catalyst. These results indicated that the hydrogen supply from NiW sulfide to the acid site was not fast enough to prevent retrogressive reactions of partially hydrogenated polycyclic aromatic compounds. It was inferred that a closer relationship between the active sites of hydrogenation and cracking was needed for the improvement of bifunctional catalysts in heavy-oil upgrading.

Key Words: **hydrocracking; tetralin; zeolite; NiW/USY; catalytic bifunctionality.**

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1. INTRODUCTION

Much effort is being devoted to improving petroleum-refining processes in response to wide concern about the environment. For this reason, increasing attention is being paid to the development of hydrocracking processes that can effectively convert heavy oils into high-quality diesel fuel fractions. The hydrocracking processes, unlike those in hydrotreating, require the use of bifunctional catalysts possessing both hydrogenation and hydrocracking functions. In the early stage of the hydrocracking process development, amorphous silica–alumina supports were predominantly used for the hydrocracking function. As zeolite technology improved, the crystalline zeolite replaced the amorphous supports. Zeolite has great advantages over amorphous silica–alumina: (i) high activity, (ii) low coke formation, and (iii) high NH_3 resistance (1, 2).

Zeolite-supported catalysts, however, still have a problem of deactivation by active-site poisoning and coke deposition during the reaction of heavy feedstock, in particular when the feedstock contains residues. To minimize these problems, most hydrocracking processes are equipped with a hydrotreatment unit ahead of the hydrocracking unit (1, 2). This greatly enhances the hydrocracking function of zeolite-based catalysts because the hydrotreated feedstock contains much less catalyst-poisoning material and is partially hydrogenated (3).

The purpose of the present study was to investigate ways of further improving zeolite-based hydrocracking catalysts in terms of the catalyst deactivation. For this purpose, we investigated the hydrocracking reaction mechanisms of tetralin with a partially hydrogenated polycyclic aromatic structure as a model compound representing heavy petroleum fractions. Although there have been reports on the cracking of tetralin over zeolite-based catalysts, most of the studies were carried out under catalytic-cracking conditions, namely at high temperatures and low hydrogen partial pressures (4–6). Lemberton *et al.* (7) reported hydrocracking of tetralin over NiMo/Y-zeolite at a relatively low temperature. However, the product distribution was not analyzed in sufficient detail to determine the reaction mechanisms.

In the present study, we performed hydrocracking of tetralin under typical hydrocracking conditions, at moderate temperatures and high hydrogen pressures, over an ultra-stable-Y (USY) zeolite-supported NiW sulfide catalyst. USY zeolite was selected due to its superiority over other kinds of zeolites in hydrocracking reactions (8, 9). The reaction mechanisms were studied by detailed analyses of the reaction products in reaction periods ranging from 3 to 180 min. On the basis of the reaction mechanisms, we discuss unfavorable reaction paths that lead to

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0021-9517/99 $30.00

coke formation and catalyst deactivation. In addition, the role of the hydrogenation function is discussed by comparing the reaction mechanisms over zeolite catalysts with and without NiW sulfide. Finally, we propose possible measures to minimize unfavorable retrogressive reactions over bifunctional hydrocracking catalysts during heavy-oil hydrocracking reactions.

2. EXPERIMENTAL

2.1. *Catalysts*

USY zeolite with a lattice Si/Al ratio = 8.4 was supplied by the Tosoh Corp. After the zeolite powder was sieved, the fraction between 75 and 250 μm was used for catalyst preparation. The loading of NiW (NiO = 3.5 wt%; WO_3 = 24.0 wt%) was performed by the incipient wetness method using a mixed solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6[H_2W_{12}O_{40}]$. After impregnation, the catalyst was dried in air at 383 K for 12 h, followed by calcination at 773 K for 3 h. As a reference catalyst without a hydrocracking function, an Al_2O_3-supported NiW catalyst with the same Ni and W loading was prepared. Prior to the model reaction and characterization, each of the calcined NiW catalysts (1.5 g) was sulfided with a flow of 5% H_2S/H_2 gas (150 ml/min) under atmospheric pressure for 2 h at 673 K. The temperature was raised from room temperature to 673 K for 1 h. After sulfidation, 5% H_2S/H_2 gas was replaced by N_2 gas when the temperature went down to room temperature. The catalyst was then transferred into a glass vial under a flow of N_2 gas.

The physical properties of the catalysts were determined using the N_2 isotherm measured on a Micromeritics ASAP 2010 system at 77 K. The surface area was calculated by the BET equation. The external surface area excluding the micropore surface was calculated by the *t*-plot method. The mesopore volume was calculated by the BJH equation.

The acid strength distributions of the catalysts were measured by NH_3 temperature-programmed desorption (NH_3-TPD) using a BEL-Japan TPD-1S system with a quadrupole mass spectrometer. After being preheated at 773 K under a He flow, each sample was treated with a flow of 10% NH_3/He for 20 min. Physisorbed NH_3 was removed by evacuation at 373 K for 1 h. The TPD spectrum was obtained by heating the sample under a He flow from 373 to 873 K at a heating rate of 10 K min^{-1}.

The dispersion of NiW sulfide was estimated by the chemisorption of NO using a pulse-type reactor with a TCD detector. After the catalyst was sulfided under the same conditions as described above, the physisorbed H_2S was removed by flowing He at 673 K for 0.5 h. After the catalyst cooled to 303 K, pulses of 9.1×10^{-6} mol of NO gas were introduced to the catalyst at intervals of 2 min until the catalyst surface was saturated by NO. The metal dispersion was calculated by dividing the amount of the adsorbed NO by that of W. The amounts of deposited coke after the model reactions were determined using a CHN recorder (Yanako MT-5). Before the analysis, the spent catalysts were washed with decalin using an ultrasonicator for 10 min followed by drying at 353 K.

2.2. *Model Reaction*

Tetralin and decalin (a mixture of *cis*- and *trans*-decalin) in the present study were commercially available reagents (Tokyo Kasei Kogyo Co., Ltd.) used without further purification. The reactions were performed using a 50-ml batch-type reactor with an electric furnace and a rocking system. The experimental conditions were as follows: model compounds, 5 ml; catalyst, 0.3 g; initial hydrogen pressure, 2–10.2 MPa (cold charge); reaction temperature, 523–623 K; reaction time, 3–180 min. Immediately after the model compound and catalyst were introduced into the reactor, the reactor was purged by H_2 gas to avoid the possible oxidation of the catalyst. Each reaction temperature could be attained within 2 min after the autoclave was inserted into the preheated electric furnace.

The liquid products were identified and determined using gas chromatography with a mass spectrometer (Hewlett-Packard 5970) and an FID detector (Hewlett-Packard 6890), employing methylsilicon capillary columns (Hewlett-Packard #1, 0.20 mm × 25 m). The gas products were determined using a gas chromatograph with a TCD detector (Hewlett-Packard 6890). The yield of each gas product was obtained as a percent of the initial reactant weight using the molar sensitivity of each product. The yield of each liquid product was at first calculated as a percent of the total liquid products using the integrated FID signals and then corrected on the basis of the total product weight including gaseous products.

3. RESULTS

3.1. *Preliminary Experiments*

The physical properties of the catalysts are listed in Table 1. Loading of NiW sulfide decreased the surface area

TABLE 1

Physical Properties of Catalysts

Catalyst	BET surface area (m^2/g)	*t*-Plot external surface area (m^2/g)	Mesopore volume (ml/g)[a]	Metal dispersion NO/W (mol/mol)
USY	621.3	75.0	0.145	—
NiW/USY	453.1	63.6	0.065	0.021
NiW/Al_2O_3	152.3	136.9	0.461	0.061

[a] Mesopore diameter: 17–3000 Å, calculated by the BJH method.

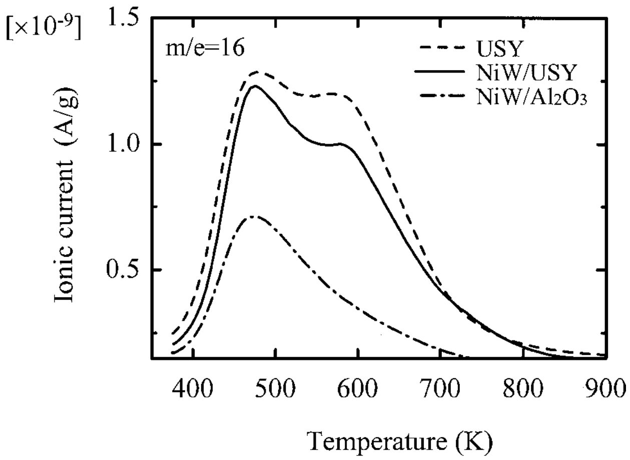


FIG. 1. NH_3-TPD profiles of the catalysts.

and pore volume of USY. In particular, the mesopore volume was significantly decreased. Figure 1 shows the NH_3-TPD profiles of the catalysts. The TPD profile of NiW/USY was almost equal to that of NiW/USY. Thus, NiW loading changed the physical properties but not the acidic properties of USY, indicating that the major part of NiW sulfide was not dispersed into micropores but resided in the mesopores. The dispersion of NiW sulfide over NiW/USY was almost one-third of that over NiW/Al_2O_3.

Figure 2 shows the changes in tetralin conversion to all species with reaction temperature over USY and NiW/USY. The conversion over NiW/USY was slightly higher than that over USY at each temperature. However, the difference between the two catalysts was relatively small. At 623 K, the conversion over NiW/Al_2O_3 was about 40%, close to that over NiW/USY. A blank test reaction without catalysts yielded no hydrocracked products except some impurities originally contained in the tetralin. Hence, to simplify discussion on product selectivity, all reactions reported hereinafter were performed at 623 K.

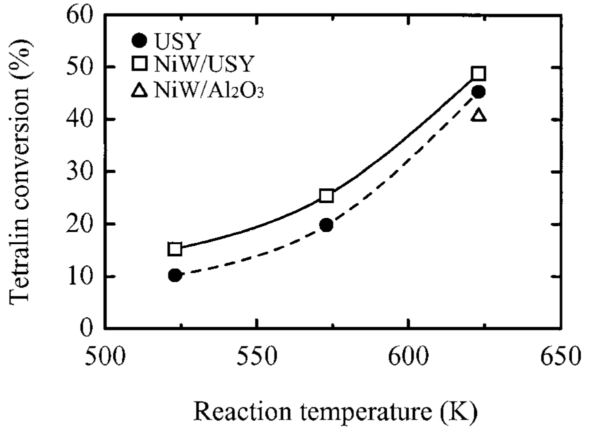


FIG. 2. Tetralin conversion to all species over the catalysts at various reaction temperatures. Reaction time, 1 h; initial H_2 pressure, 6.1 MPa. The reaction rates and TOF over the catalysts are as follows. Reaction rates (mol/(s g-cat)): USY, 3.6×10^{-6} at 523 K, 7.0×10^{-6} at 573 K, and 3.8×10^{-5} at 623 K; NiW/USY, 5.4×10^{-6} at 523 K, 9.0×10^{-6} at 573 K, and 4.5×10^{-5} at 623 K; NiW/Al_2O_3, 2.4×10^{-5} at 623 K. TOF (molecules/(s hydrogenation active site)): NiW/USY, 2.4×10^{-1} at 523 K, 4.1×10^{-1} at 573 K, and 2.0 at 623 K; NiW/Al_2O_3, 3.7×10^{-1} at 623 K.

3.2. *Product Distribution in Tetralin Hydrocracking*

As shown in Fig. 3, the GC-FID and GC-MS analyses identified more than 300 compounds in the hydrocracked products of tetralin over USY or NiW/USY. We classified these products into several groups so that the catalytic functionality could be treated according to the yields of the grouped products. The products were first divided into "light compounds" and "heavy compounds," according to whether their retention time was shorter or longer than that of tetralin, respectively. The light compounds were further classified into 6 groups: (i) alkane gas; (ii) benzene and alkylbenzene; (iii) monocycloparaffin (cyclohexane, etc.); (iv) decalin; (v) decalin isomer (methylperhydroindene, etc.); (vi) indan and methylindan. The compounds in (i), (ii), and (iii) were defined as hydrocracked products.

The major bicyclic heavy compounds were (vii) naphthalene and (viii) alkyltetralin. Other heavy compounds consisted of (ix) tricyclic compounds, 1,2,3,4,5,6,7,8-octahydrophenantharene (OHP) and anthracene (OHA); (x) OHP and OHA isomers; (xi) tetrahydro phenanthrene (THP) and anthracene (THA); (xii) a group of heavy compounds with mass numbers smaller than 260, mainly alkyldecalin-type compounds; (xiii) products with mass numbers higher than 260. Most of the compounds in group (xiii) were identified by their mass spectra as phenylbutyltetralin (PBT: $m/e = 264$) with small amounts of related compounds (PBTs: $m/e = 262$ and 266). It should be noted that almost no phenanthrene or anthracene was detected.

Figure 4 shows the total conversion and product distribution according to the above groupings over USY, NiW/USY, and NiW/Al_2O_3. Over both USY and NiW/USY, the selectivity to light compounds was lower than that to heavy compounds. The effect of NiW sulfide loading was increased selectivity to light compounds. In particular, the production of naphthalene was significantly suppressed by NiW sulfide. In addition, NiW sulfide loading increased the yields of hydrocracked products, decalin and decalin isomers.

Composition of the products over NiW/Al_2O_3, mainly decalin with small proportions of heavy compounds, was completely different from that over USY and NiW/USY (Fig. 4). This indicates that NiW sulfide functions solely as a hydrogenation catalyst, not as a hydrocracking or isomerization catalyst, under the above reaction conditions. In summary, the results in Fig. 4 indicate that the USY-based catalysts yield larger proportions of heavy compounds than light compounds, even with the NiW sulfide loading. To elucidate the formation and elimination mechanisms of the

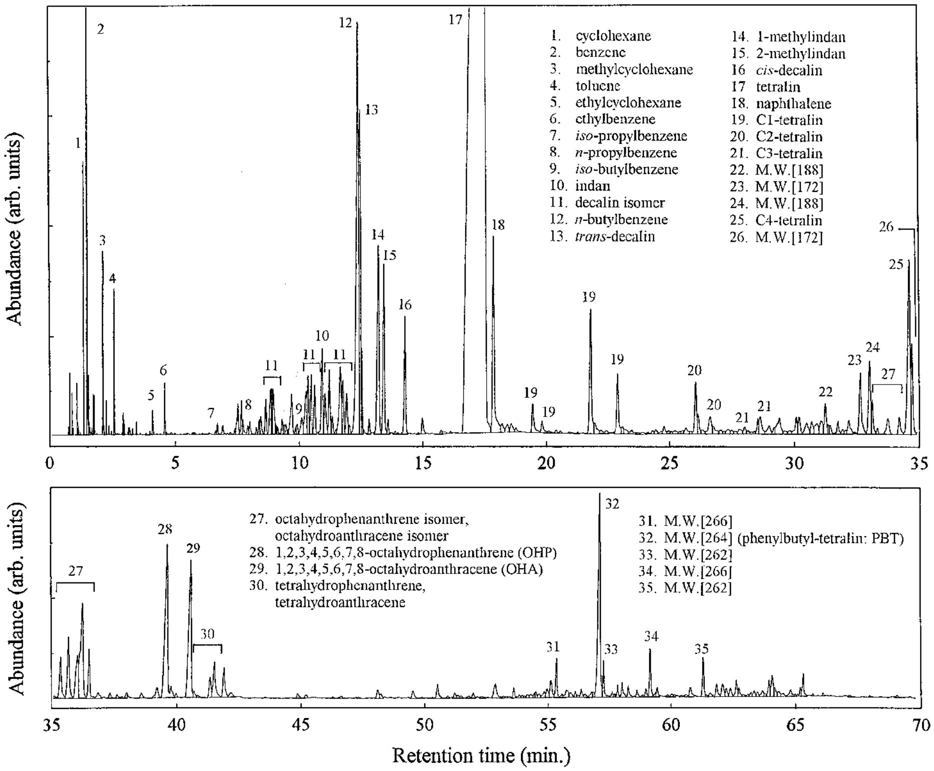


FIG. 3. FID gas chromatogram of a tetralin-hydrocracked product over NiW/USY. Reaction temperature, 623 K; reaction time, 1 h; initial H_2 pressure, 6.1 MPa.

heavy compounds, the reaction time was then varied from 3 to 180 min.

3.3. *Changes in Product Distribution with Reaction Time*

Figure 5 shows the changes in total conversion and yield of hydrocracked products with reaction time over USY and NiW/USY. The conversion over USY was almost the same

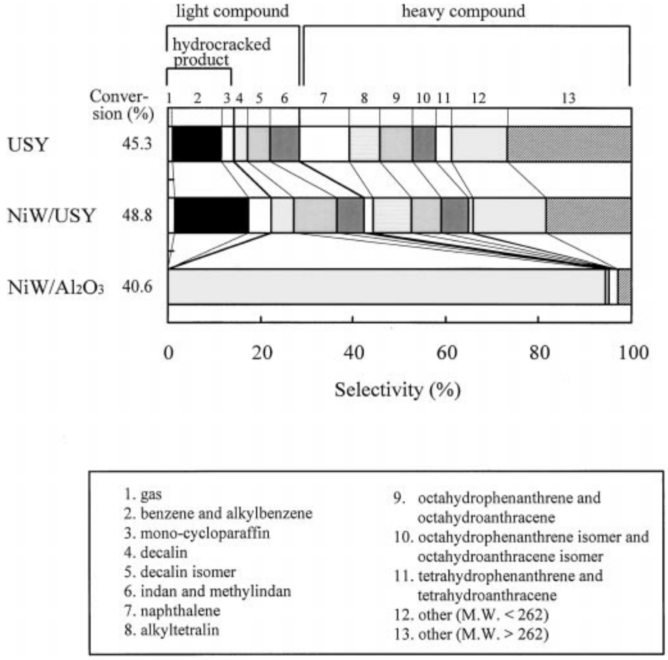


FIG. 4. Conversion and product distribution in the tetralin hydrocracking reaction. Reaction temperature, 623 K; reaction time, 1 h; initial H_2 pressure, 6.1 MPa.

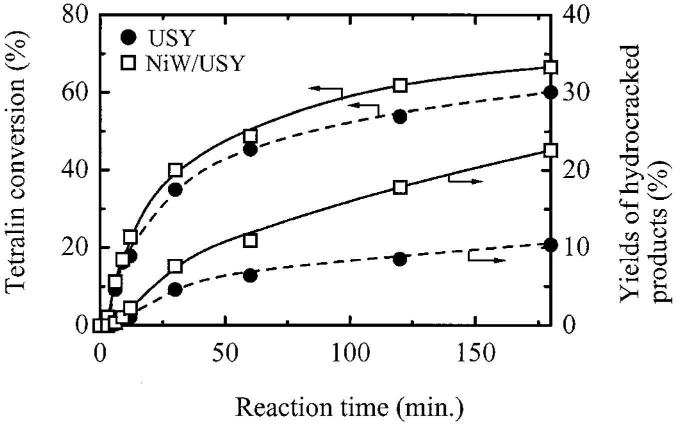


FIG. 5. Tetralin conversion and yield of hydrocracked products against reaction time over USY and NiW/USY. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa. The reaction rates (mol/(s g-cat)): USY, 3.8×10^{-5}; NiW/USY, 4.5×10^{-5}.

TABLE 2

The Initial Reaction Rate of Tetralin Hydrocracking

	Total reaction		Reaction to hydrocracked products	
Catalyst	Rate (mol/(s g-cat))	TOF (molecules/(s N^a))	Rate (mol/(s g-cat))	TOF (molecules/(s N^a))
USY	3.8×10^{-5}	—	2.5×10^{-6}	—
NiW/USY	4.5×10^{-5}	2.0	2.7×10^{-6}	1.2×10^{-1}

[a] *N*: The number of hydrogenation active sites in NiW/USY was estimated by NO chemisorption.

as that over NiW/USY for the first 10 min and slightly lower in a longer reaction. The reaction rates shown in Table 2 were calculated using the conversion of tetralin and the yield of hydrocracked products during the initial periods of the reaction. The initial reaction rate of tetralin over USY was not very different from that over NiW/USY. The initial production rate of hydrocracked products over USY was also similar to that over NiW/USY. In contrast, significant differences were observed between the yields of hydrocracked products over the two catalysts in longer reactions. The effect of the NiW sulfide loading was small at the beginning of the reaction and gradually increased over time, in particular, in terms of the yields of hydrocracked products.

It should be noted that the hydrocracking and hydrogenation reactions decrease the H_2 partial pressure during the reaction and affect the reaction rates. The final H_2 pressure after 180 min of the reaction over NiW/USY was 3.9 MPa. This indicates that the rate at the end of the reaction in Fig. 5 was reduced by as high as about 35%, if one assumes the first-order dependence of the rate on the H_2 partial pressure. Also, the yields of hydrogenated products over NiW/USY in Figs. 8 and 9 were suppressed to some extent by the decrease in the H_2 partial pressure.

To examine the effect of mass transfer limitation, the Thiele modulus was estimated using the following equation,

$$\Phi = (R^2 r)/(D_{\mathrm{eff}} C_{\mathrm{s}}),$$

where R is the radius of the particle, r is the reaction rate, D_{eff} is the effective diffusion coefficient, and C_{s} is the surface concentration of the reactant (10). R was calculated at 8×10^{-3} (cm), and r was calculated at 1.6×10^{-5} (mol/(s cm^3)) from the initial reaction rate over NiW/USY and the density of the catalyst (0.35 g/cm^3). D_{eff} was assumed to be 1.6×10^{-4} (cm^2/s) using the result on the hydrocracking of decalin over Pd/mordenite by Beecher *et al.* (11). C_{s} was calculated at 7.4×10^{-4} (mol/cm^3) from the initial concentration of tetralin. Thus, Φ was calculated at 9×10^{-3}, which was smaller than 0.1. This indicates that the reaction was not controlled by pore diffusional limitation.

For detailed analysis, the yield of each product group was plotted as a function of reaction time in Figs. 6–9. A comparison of Figs. 6 and 7 indicates that the product distribution over NiW/USY was similar to that over USY in short reactions. Over both catalysts, the most abundant products were PBT and PBTs (◆, M.W. > 260 in Fig. 6), of which the yield was 1.6% at 3 min, reaching 7–8% at 9 min. The second most abundant products were OHA and OHP. Decalin and naphthalene were also produced at the very beginning, although their proportions were relatively small. In the next stage,

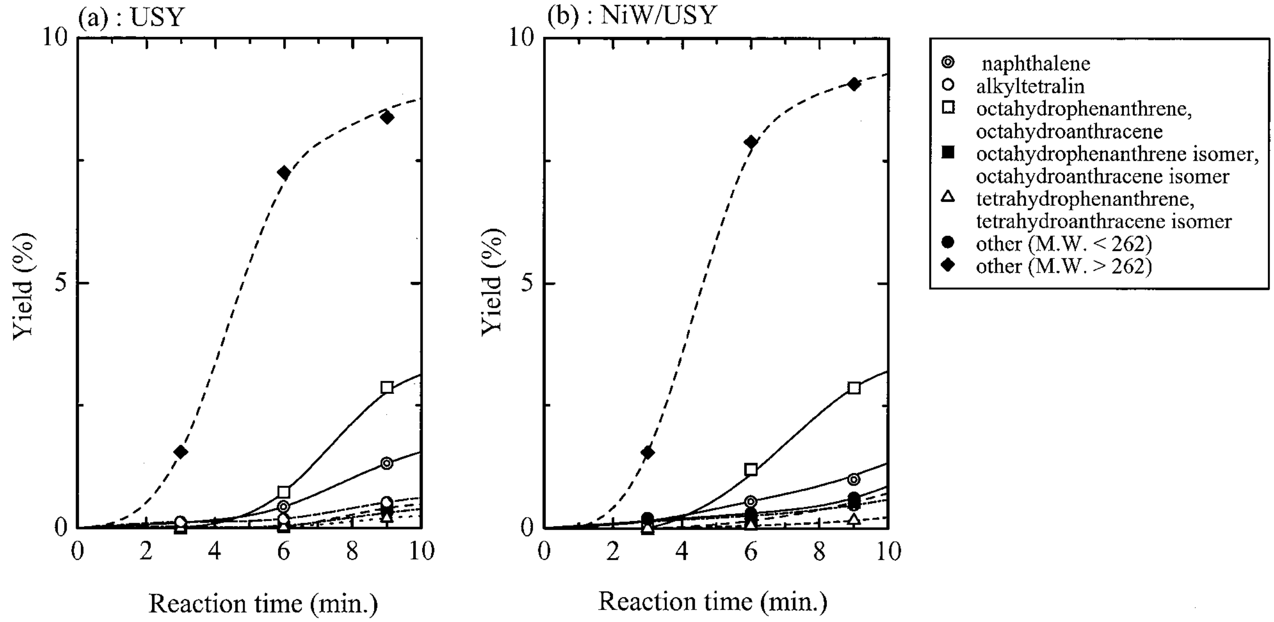


FIG. 6. Changes in product distribution with reaction time over (a) USY and (b) NiW/USY. (I) Heavy compounds produced with reaction times of 0–9 min. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

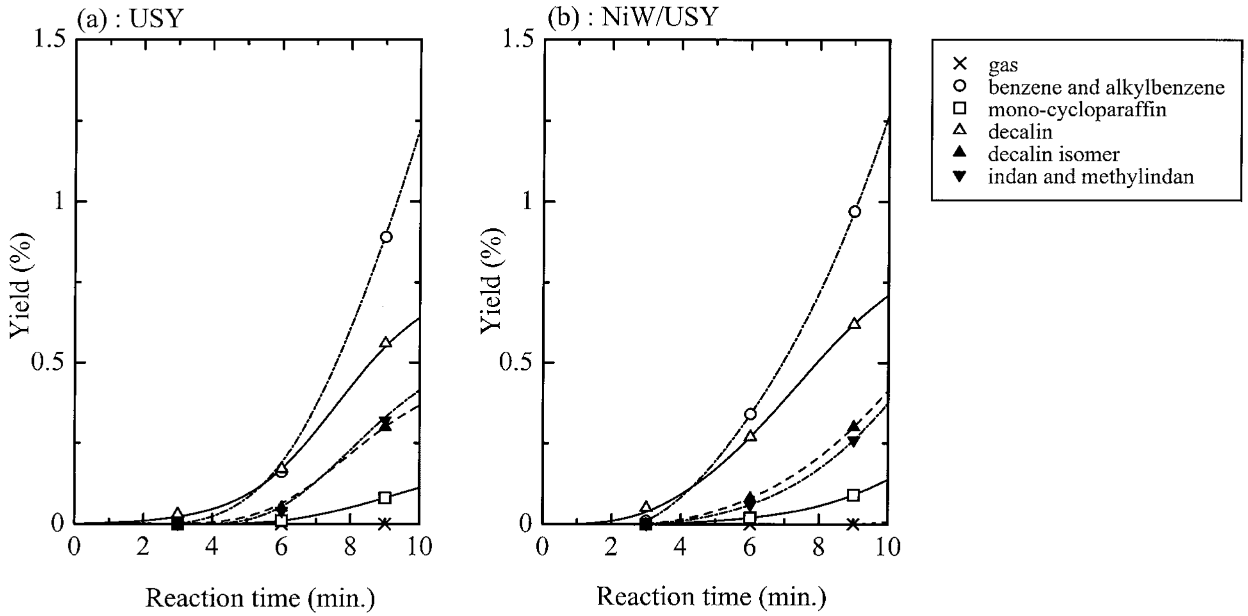


FIG. 7. Changes in product distribution with reaction time over USY (a) and NiW/USY (b). (II) Light compounds produced with reaction times of 0–9 min. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

hydrocracked products, benzene and alkylbenzene (○, in Fig. 7), were formed with increasing reaction time, after 6 min. Benzene and *n*-butylbenzene were the predominant hydrocracked products as shown in Table 3. In particular, benzene was selectively produced at the beginning of the reaction. No gaseous product was detected in the products in reactions up to 9 min (Table 4).

Significant differences were observed between the product distributions over USY and NiW/USY in longer reactions (Figs. 8 and 9). The yield of PBT and PBTs (◆) over USY continued to increase up to 180 min (Fig. 8a), whereas that over NiW/USY reached a maximum at 15 min and then decreased (Fig. 8b). Over NiW/USY, the yields of hydrocracked products (× , ○, □) increased gradually with reaction time up to 180 min (Fig. 9a). The yields of these products over USY also increased but at a much lower rate after the first 10 min (Fig. 9b). As a result, the total yield of hydrocracked products over NiW/USY was more than twice that over USY.

Similar trends were observed in the yields of hydrogenated products. Over NiW/USY, the yield of decalin (△, in Fig. 9) reached a maximum at 120 min and remained constant thereafter. In contrast, that over USY reached a maximum at 30 min and then decreased. The yield of naphthalene (◎, in Fig. 8) over USY gradually increased up to 120 min, while that over NiW/USY was at its maximum at 30 min. These results indicate that NiW/USY continuously produced decalin, which was subsequently subjected to hydrocracking or isomerization, while USY produced decalin only at the beginning of the reaction.

3.4. *Hydrogen Species Involved in Tetralin Hydrocracking*

Figure 10 shows the changes in product distribution with hydrogen pressure. Product distribution over USY was

TABLE 3

Yields of Alkylbenzene for 9 min and 1 h of Reactions

	USY		NiW/USY	
Reaction time	9 min	1 h	9 min	1 h
Benzene	0.709	2.392	0.782	3.590
Toluene	0.019	0.132	0.022	0.160
Ethylbenzene	0.032	0.099	0.032	0.109
Xylene	0.002	0.010	0.002	0.007
n-Propylbenzene	0.006	0.049	0.005	0.043
Isopropylbenzene	0.000	0.006	0.001	0.009
n-Butylbenzene	0.160	1.075	0.162	2.091
Isobutylbenzene	0.004	0.043	0.006	0.080

TABLE 4

Yields of Gaseous Products for 9 min and 1 h of Reactions

	USY		NiW/USY	
Reaction time	9 min	1 h	9 min	1 h
Methane	0.00	0.00	0.00	0.00
Ethane	0.00	0.00	0.00	0.00
Propane	0.00	0.10	0.00	0.17
n-Butane	0.00	0.03	0.00	0.06
Isobutane	0.00	0.03	0.00	0.05

Note. Olefin compounds were not detected.

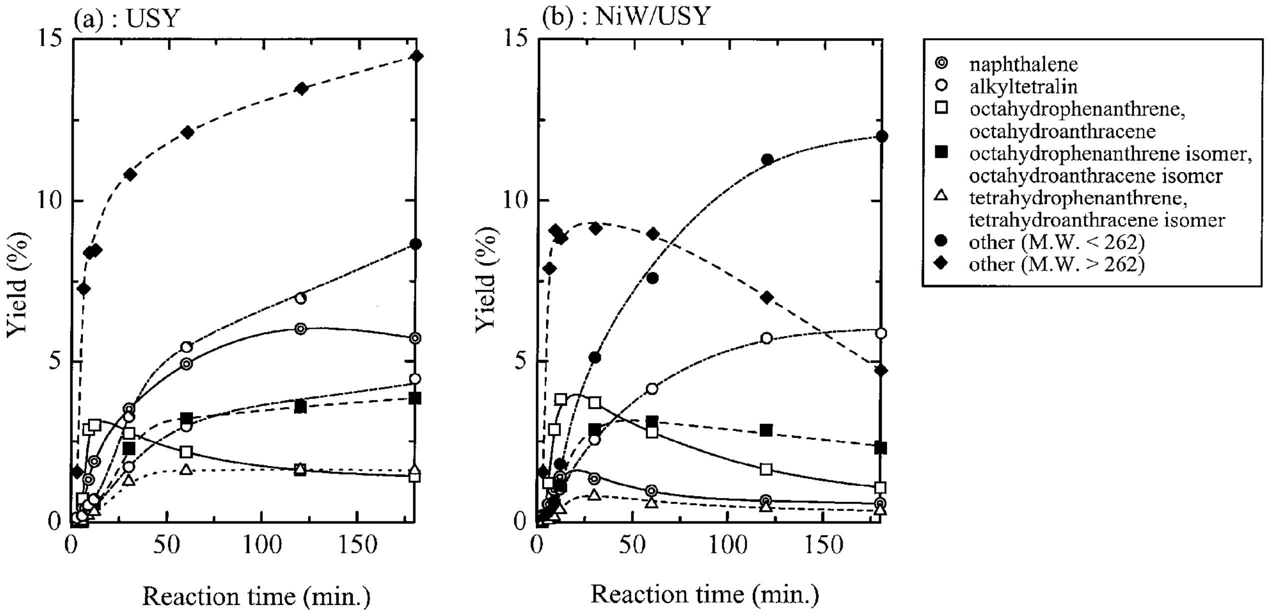


FIG. 8. Changes in product distribution with reaction time over USY (a) and NiW/USY (b). (III) Heavy compounds produced with reaction times of 0–120 min. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

found to be independent of hydrogen pressure (Fig. 10a). This indicates that hydrocracking over USY was catalyzed without the involvement of gaseous hydrogen and that hydrogen in the reaction was supplied by the dehydrogenation of tetralin. However, over NiW/USY, hydrogen partial pressure significantly affected the yields of most products except indan and methylindan (▼) (Fig. 10b). High hydrogen pressures increased the yields of hydrogenated and hydrocracked products and decreased yields of heavy compounds. Thus, NiW sulfide provides dissociatively adsorbed hydrogen for hydrogenation and hydrocracking.

Figure 11 shows the product distribution over physical mixtures of USY and NiW/Al_2O_3. The yields of hydrocracked products over the mixtures increased with an increasing proportion of NiW/Al_2O_3. The product distribution over the mixture containing 0.2 g of NiW/Al_2O_3 was

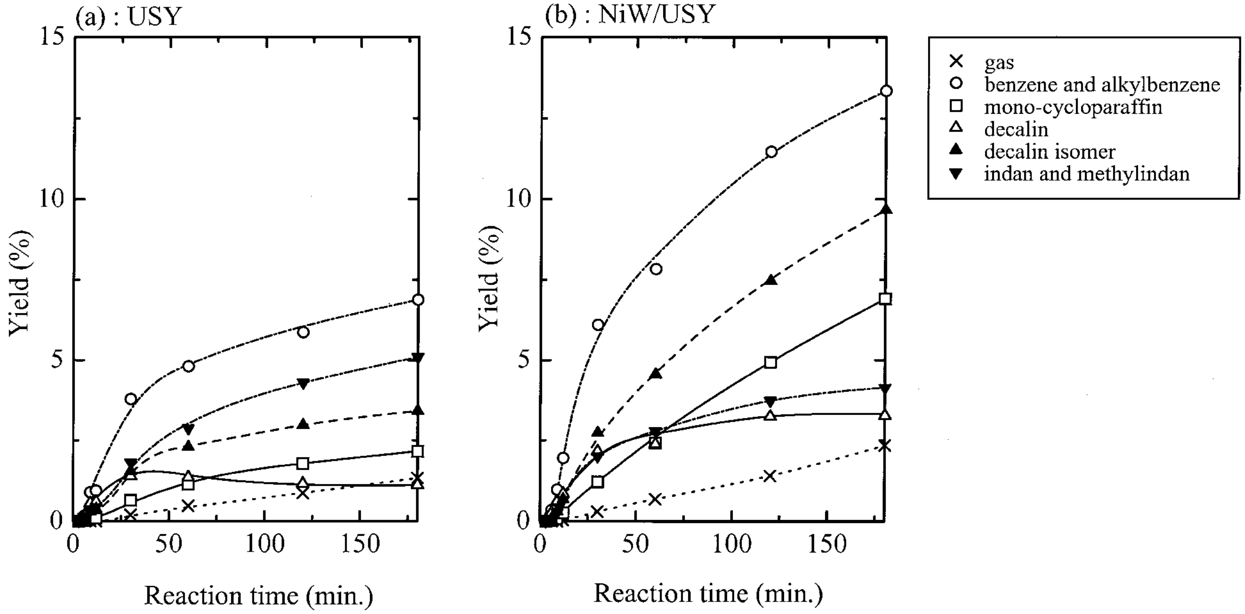


FIG. 9. Changes in product distribution with reaction time over USY (a) and NiW/USY (b). (IV) Light compounds produced with reaction times of 0–120 min. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

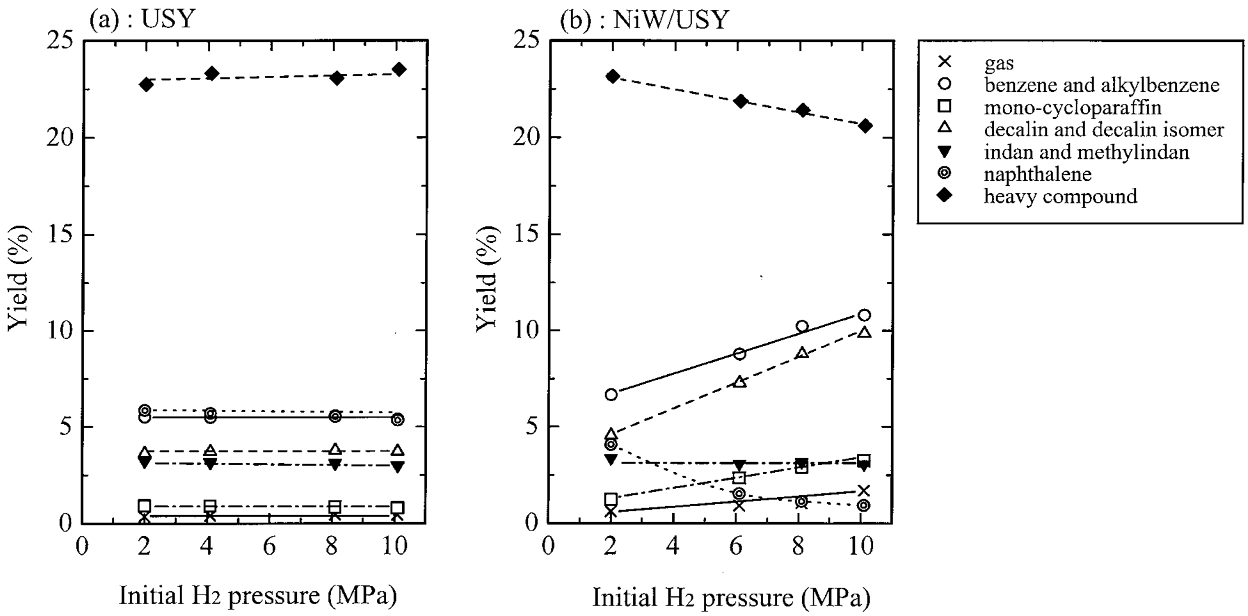


FIG. 10. Changes in product distribution with initial H_2 pressure over USY (a) and NiW/USY (b). Reaction temperature, 623 K; reaction time, 1 h.

almost the same as that over 0.3 g of NiW/USY. This indicates no strong synergy beyond physical contact between the hydrogenation-active sites on NiW sulfide and the acid sites on USY.

Figure 12 shows the changes in conversion of decalin over USY and NiW/USY with reaction time. Under the same reaction conditions, the conversion of decalin was higher than that of tetralin over both USY and NiW/USY. The initial reaction rate over NiW/USY was almost twice as high as that over USY. Figure 13 shows the product distribution classified into four groups: (i) decalin isomers; (ii) gases; (iii) liquid hydrocracked products; (iv) heavy compounds. The amounts of heavy compounds over both USY and NiW/USY were smaller than those in tetralin hydrocracking. Over USY, the total conversion and yields of decalin isomers were almost constant after 60 min, while the yields of gaseous products and heavy compounds gradually increased up to 120 min. Over NiW/USY, decalin isomers were produced at first and then converted into hydrocracked products.

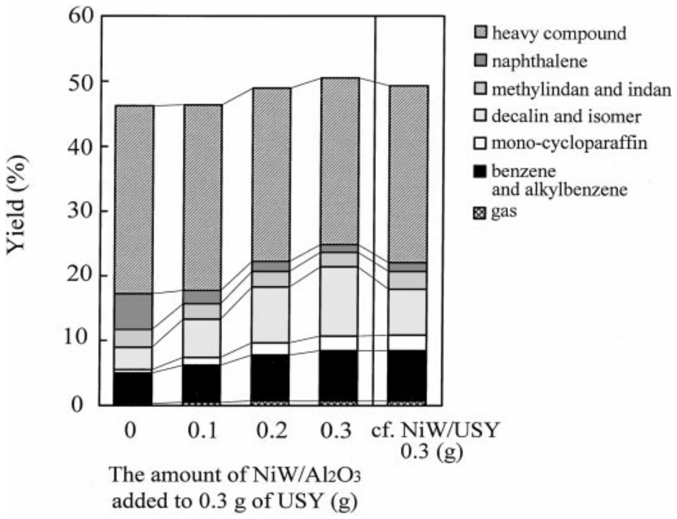


FIG. 11. Total conversion and product distribution over the physical mixture of USY (0.3 g) and NiW/Al_2O_3 (0.1–0.3 g). Reaction temperature, 623 K; reaction time, 1 h; initial H_2 pressure, 6.1 MPa.

3.5. *Coke Deposition on the Spent Catalysts*

Figure 14 shows that the amounts of deposited carbon on the two catalysts in the hydrocracking of tetralin were independent of the reaction time. Thus, we assume that coke

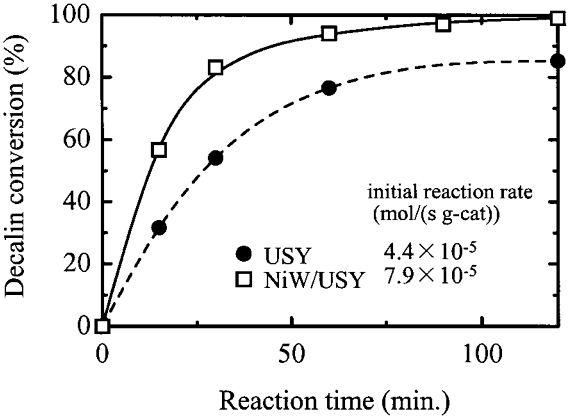


FIG. 12. Decalin conversion over USY and NiW/USY. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

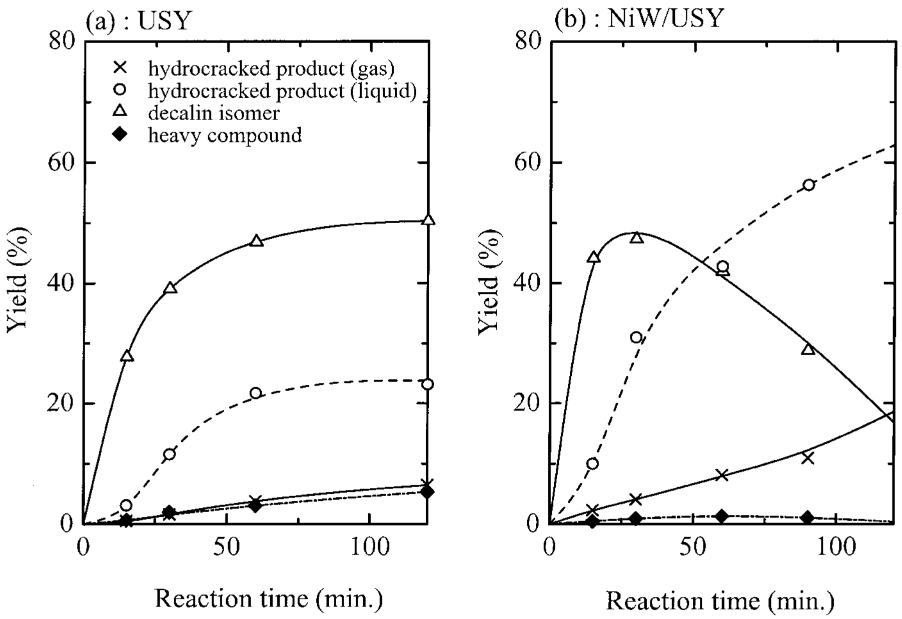


FIG. 13. Product distribution in the decalin hydrocracking over USY (a) and NiW/USY (b). Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

formation took place only at the beginning of the reaction and did not significantly affect the catalytic activity and selectivity of the catalysts during subsequent reactions. In the hydrocracking of decalin, a similar trend was observed, although the amounts of carbon deposited were smaller than those in the hydrocracking of tetralin (Fig. 15).

4. DISCUSSION

4.1. *Reaction Paths of Tetralin over Bifunctional Catalysts*

The above results can be summarized as follows: (i) The yields of heavy compounds were larger than those of light compounds over both USY and NiW/USY. (ii) At the beginning of the reaction (up to 9 min), the conversion and product distribution over NiW/USY were similar to those over USY. (iii) At the beginning of the reaction (up to 9 min), PBT and PBTs were the most abundant products, followed by tricyclic compounds, OHA and OHP. (iv) In longer reactions, the superiority of NiW/USY over USY was observed. NiW loading enhanced the production of hydrocracked and hydrogenated products and suppressed that of dehydrogenated products. (v) Two hydrogen species were involved in the hydrocracking. Over USY, hydrogen was supplied solely by the dehydrogenation of tetralin. In addition, dissociatively adsorbed hydrogen on

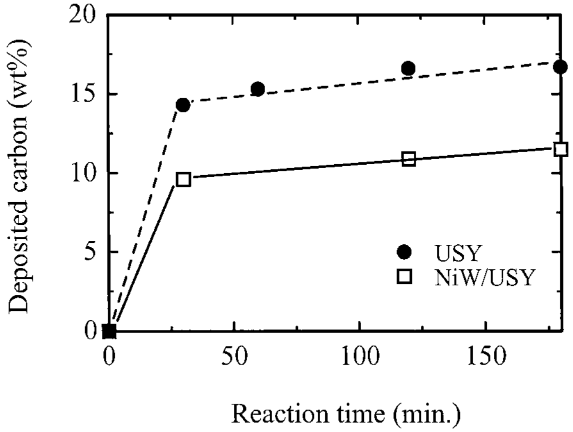


FIG. 14. Amounts of carbon deposited on the catalyst over USY and NiW/USY in tetralin hydrocracking. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.

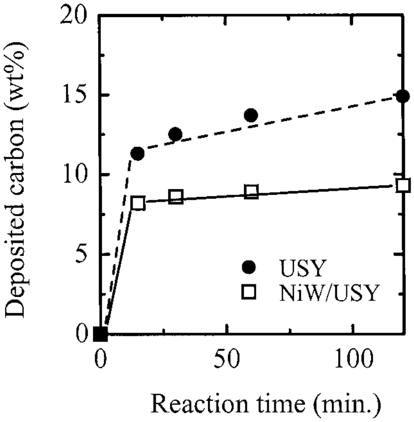
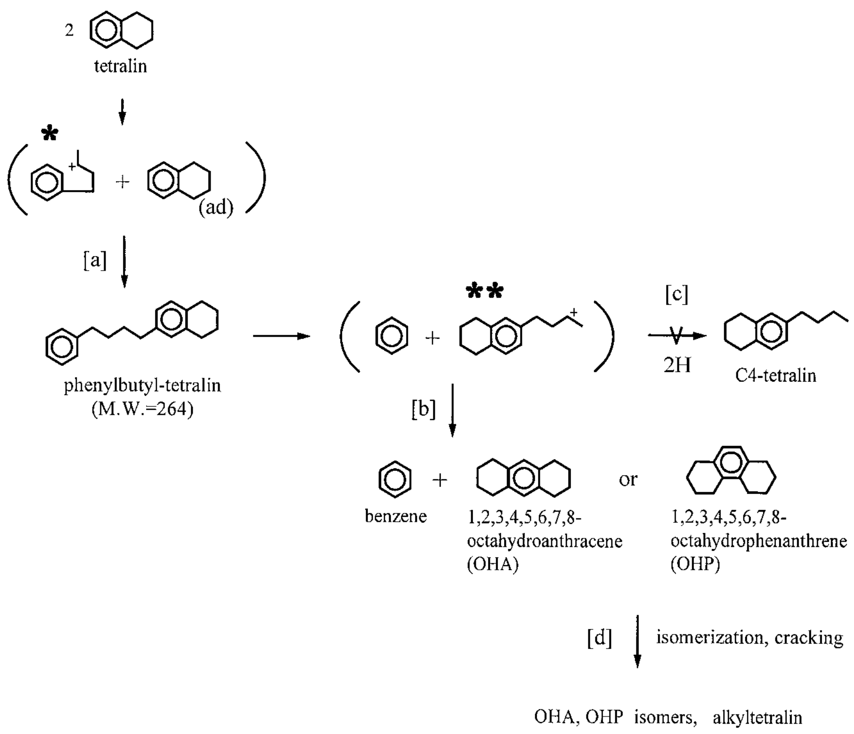


FIG. 15. Amounts of carbon deposited on the catalyst over USY and NiW/USY in decalin hydrocracking. Reaction temperature, 623 K; initial H_2 pressure, 6.1 MPa.



SCHEME 1

NiW sulfide was supplied over NiW/USY. (vi) The reactions over physical mixtures of NiW/Al$_2$O$_3$ and USY suggest no strong synergy between hydrogenation activities and acid sites.

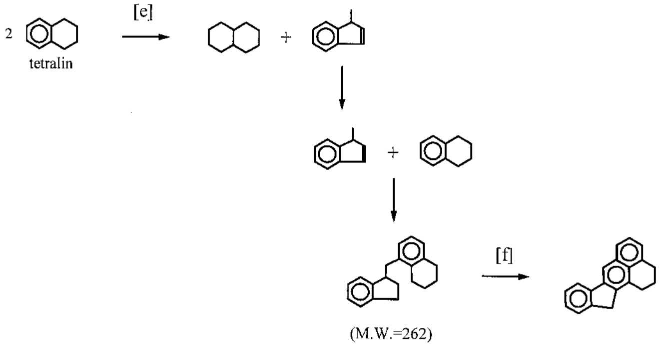
Results (ii) and (iv) suggest that the reaction paths in the initial reaction period were different from those later in the reaction. The two paths are discussed separately below.

Initial reaction period (up to 9 min). Results (i) and (iii) indicate that the reactions during the initial period yield PBT which are subsequently converted into OHA or OHP. Thus, we propose Scheme 1 as the major reaction path at the initial stage. The first step in the reaction is the formation of PBT from two tetralin molecules adsorbed on the acid sites of USY [a]. PBT consecutively decomposes into benzene and the tetrahydronaphthylbutyl cation. The latter is not stabilized to yield butyltetralin [c] but is converted into OHA or OHP [b]. OHA and OHP are subsequently isomerized or cracked to alkyltetralin [d]. Parallel to the hydrocracking in Scheme 1, there are many possible paths that yield polycyclic compounds from phenylbutyl cations (*) or tetrahydronaphthylbutyl cations (**) by chain reaction mechanisms. In particular, the tetrahydronaphthylbutyl cation is very likely a coke precursor that results in coke formation on the catalysts in the initial period as shown in Fig. 14.

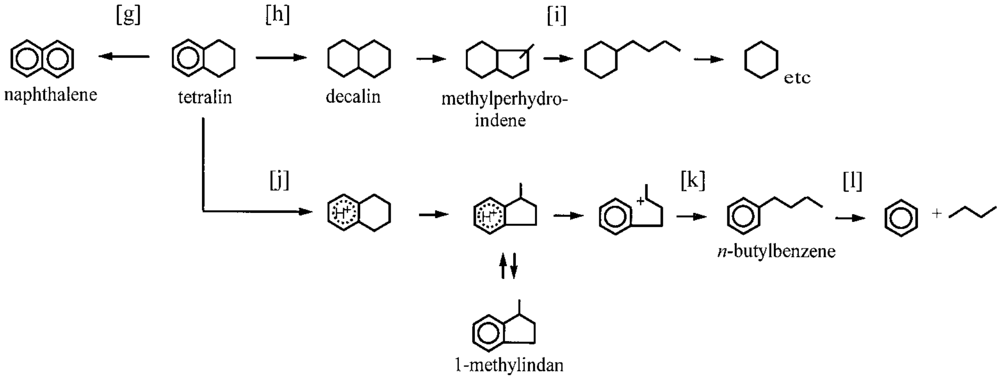
In addition to the above paths, the production of PBTs suggests the existence of other coke formation paths (Scheme 2). For example, PBTs with *m/e* of 262 can be produced from tetralin by the addition of methylindene which is produced by the disproportionation of two tetralin molecules [e]. The molecule with an *m/e* of 262 is easily converted into a coke precursor as shown in [f].

Previous reports on the cracking of tetralin over zeolite catalysts (4–6) did not give clear evidence of PBT production. This may be due to high reaction temperatures (673 K (5, 6) and 733–755 K (4)) in these studies because PBT is readily converted to benzene and coke on the catalyst.

In addition to the above “bimolecular” reaction mechanism, “monomolecular” hydrocracking reactions shown in Scheme 3 proceed over USY. After the fast dehydrogenation [g] and hydrogenation [h] of tetralin, cycloparaffinic rings open via methylperhydroindene [h, i]. Also, direct



SCHEME 2



SCHEME 3

ring-opening via methylindan to *n*-butylbenzene [j] proceeds, followed by further cracking to benzene and butane [k]. Result (iii) indicates that monomolecular hydrocracking is the minor path during the initial reaction period.

Longer reaction period (after 9 min). The obvious effect of NiW sulfide loading is observed in reactions longer than 10 min, indicating the important role of the hydrogenation function of NiW sulfide. Over NiW/USY, the yield of naphthalene significantly decreases over time parallel to an increasing yield of decalin (Figs. 8 and 9). The aromatic rings are hydrogenated over NiW/USY by using the dissociatively adsorbed hydrogen from the gaseous phase (results (v)). As a result, the hydrocracking path shown in Scheme 3 is dominant over NiW/USY in longer reactions. In the initial reaction period, benzene is produced via PBT and PBTs as shown in Scheme 1 [b]. Subsequently, however, benzene is produced via butylbenzene (Scheme 3 [1]) as evidenced by the production of butylbenzene and butane (Tables 3 and 4). In longer reactions, the heavy compounds produced in the initial period gradually decompose to light compounds.

4.2. *The Role of NiW Sulfide Loading on USY*

The first step of the cracking is production of phenylbutyl cations on the acid sites via either the monomolecular or bimolecular reaction scheme. Stabilization of the phenylbutyl cation by hydrogen would yield butylbenzene. However, the present results indicate that shortage of hydrogen in the initial reaction period yields PBT and PBTs by aromatic electrophilic substitution. On bifunctional catalysts, an important role of the metal sulfide is to provide hydrogen to stabilize the cations via a hydrogen spillover mechanism (12, 13). The mechanism does not work effectively to suppress aromatic electrophilic substitution in the initial reaction period.

The results of the test reactions of decalin and diphenylmethane (DPM) conducted under the same conditions provide more information on the roles of the hydrogenation function of NiW sulfide. In the case of decalin, hydrocracking starts with the formation of a cyclohexylbutyl cation. The bimolecular reactions are rare, unlike the tetralin hydrocracking, probably due to the low rate of electrophilic substitution on cycloparaffinic rings. Thus, the hydrocracking of decalin proceeds predominantly by the monomolecular reaction.

Although decalin is easily isomerized over acid sites, the yield of hydrocracked products over USY without NiW sulfide is low. This is due to the low hydrogen-donor ability of decalin compared with that of tetralin, which can supply hydrogen for hydrocracking by the dehydrogenation of naphthalene. Over NiW/USY, hydrocracked products are formed from the beginning of the reaction. These results indicate that NiW plays an essential role in hydrogen supply for the hydrocracking of decalin. In the initial period of tetralin hydrocracking, however, the effect of hydrogen supply by NiW sulfide is negligibly small.

In a previous study on the hydrocracking of DPM (14), we reported that the loading of NiW sulfide effectively prevented polymerization. The hydrogen supply from NiW sulfide was able to stabilize the intermediate benzyl cations and to yield toluene. The difference between tetralin and DPM probably arises from the reactivity of the intermediate cations. Prevention of oligomerization of tertiary phenylbutyl cations is more difficult than that of primary benzyl cations.

The above discussions indicate two roles of NiW sulfide. One is the supply of hydrogen to acid sites: a supply of hydrogen is essential for continuous hydrocracking, as shown in the reaction of decalin. In addition, the oligomerization of intermediate cations is suppressed by the dissociatively adsorbed hydrogen species at the acid sites on USY, as observed in the reaction of DPM. The other role is hydrogenation of aromatic compounds to cycloparaffinic compounds. NiW sulfide in the hydrocracking of tetralin evidently plays the latter role but does not function effectively as the hydrogen supplier to the acid sites, particularly during the initial stage of the reaction. The poor performance may be related to the low dispersion of NiW sulfide over USY as shown in Table 1.

4.3. Design of Hydrocracking Catalysts for Heavy Oils

In heavy-oil upgrading, hydrocracking is conducted as the secondary process after hydrotreatment. The feed is then rich in partially hydrogenated polycyclic aromatic compounds, such as tetralin. Scheme 1 indicates that the reaction of tetralin over bifunctional catalysts yields coke precursors via aromatic electrophilic substitution parallel to hydrocracking. OHA and OHP, which are partially hydrogenated aromatic compounds, are very likely to be subject to further electrophilic substitution that finally yields coke materials on the catalyst.

The initial period of the reaction in the present study corresponds to the "fast reaction" in continuous flow reactors, the longer reactions corresponding to the "slow reaction". The fact that the reaction proceeds via Scheme 1 at the initial stage indicates that retrogressive reactions with coke formation are faster reactions than those in hydrocracking via Scheme 3. In fact, the results shown in Fig. 14 indicate that coke forms on the catalyst in the very initial period. Other evidence of coke precursors by electrophilic substitution can be found by comparison with the reaction of decalin, in which the amounts of coke and heavy compounds formed are less than those in the reaction of tetralin.

Aromatic electrophilic substitution is attributed to the shortage of hydrogen supply to the active cations formed on the acid sites. From this point of view, strong synergy between the hydrogenation-active metal sulfides and acid sites possibly prevents aromatic electrophilic substitution. There have been several reports on metal loading methods on zeolite that can disperse the metals in micropores (15, 16) or that can enhance hydrogenation activity (17). These methods may enhance the hydrocracking activity of catalysts by more effective supply of hydrogen to the acid sites. Another solution may be found by reducing the solid acidity so that the acidity balances the hydrogenation activity of the metal sulfides. For instance, control of Si/Al ratios can change the acidity and hydrogen-transfer ability of Y-zeolite (18–20).

Finally, proper porosity of zeolite is essential in catalysts for processing heavy feed. The present USY contained relatively large mesopore volumes before the loading of NiW sulfide. However, the loading dramatically decreased the mesoporosity (see Table 1).

5. CONCLUSIONS

In the present study, hydrocracking reaction paths of tetralin over USY and NiW/USY were investigated, aimed at the improvement of zeolite-based catalysts for heavy oil hydrocracking. From the results, the following conclusions are obtained.

The major path of tetralin hydrocracking in the initial reaction period is different from that later in the reaction. During the initial reaction period, tetralin is hydrocracked via a bimolecular process over both USY and NiW/USY. Subsequently, hydrocracking is catalyzed without the formation of heavy compounds. Hydrocracking over NiW/USY is superior to that over USY only in the longer reactions.

This difference is due to the limited role of NiW sulfide in the hydrocracking of tetralin. NiW sulfide hydrogenates aromatic compounds so that the cycloparaffinic compounds produced are easily cracked over the acid sites. However, NiW sulfide cannot supply hydrogen to the acid sites fast enough to stabilize the intermediate cations. Thus, the initial reaction of tetralin proceeds via a bimolecular path, in which aromatic electrophilic substition yields polycyclic aromatic compounds that are typical coke precursors.

ACKNOWLEDGMENT

This work has been financially supported by the Petroleum Energy Center with the subsidy of the Ministry of International Trade and Industry.

REFERENCES

1. Maxwell, I. E., *Catal. Today* **1**, 55 (1987).
2. Ward, J. W., *Fuel Process. Technol.* **35**, 55 (1993).
3. Shimada, H., Yoshitomi, S., Sato, T., Matsubayashi, N., Imamura, M., Yoshimura, Y., and Nishijima, A., *Stud. Surf. Sci. Catal.* **106**, 115 (1997).
4. Mostad, H. B., Riis, T. U., and Ellestad, O. H., *Appl. Catal.* **63**, 345 (1990).
5. Townsend, A. T., and Abbot, J., *Appl. Catal. A* **90**, 97 (1992).
6. Townsend, A. T., and Abbot, J., *Appl. Catal. A* **95**, 221 (1993).
7. Lemberton, J. L., Baudon, A., Guisnet, M., Marchal, N., and Mignard, S., *Stud. Surf. Sci. Catal.* **106**, 129 (1997).
8. Kameoka, T., Masuda, K., Kinoshita, A., Sato, T., Yoshimura, Y., Shimada, H., Matsubayashi, N., and Nishijima, A., *Coal Sci. Technol.* **24**, 1479 (1995).
9. Dai, P. E., Sherwood, D. E., Jr., and Martin, B. R., *Stud. Surf. Sci. Catal.* **83**, 489 (1994).
10. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis," MIT Press, Cambridge, MA, 1970.
11. Beecher, R., Voorhies, A., Jr., and Eberly, P., Jr., *Ind. Eng. Chem., Prod. Res. Dev.* **7**, 203 (1968).
12. Stumbo, A. M., Grange, P., and Delmon, B., *Catal. Lett.* **31**, 173 (1995).
13. Roessner, F., and Roland, U., *J. Mol. Catal. A* **112**, 401 (1996).
14. Sato, K., Iwata, Y., Yoneda, T., Nishijima, A., Miki, Y., and Shimada, H., *Catal. Today* **45**, 367 (1998).
15. Okamoto, Y., *Catal. Today* **39**, 45 (1997).
16. Tatsumi, T., Taniguchi, M., Ishige, H., Ishi, Y., Murata, T., and Hidai, M., *Appl. Surf. Sci.* **121/122**, 500 (1997).
17. Cornet, D., Qotbi, M. El., and Leglise, J., *Stud. Surf. Sci. Catal.* **106**, 147 (1997).
18. Scherzer, J., *ACS Symp. Ser.* **248**, 157 (1984).
19. Bezman, R., *Catal. Today* **13**, 143 (1992).
20. Corma, A., Faraldos, M., and Mifsud, A., *Appl. Catal.* **47**, 125 (1989).