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FeS_2-Catalyzed Hydrocracking of α,ω-Diarylalkanes

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Hydrocracking reactions of α,ω-diarylalkanes (DAAs) were carried out in the presence of FeS_2 catalyst to examine the structural effect of DAAs on the reactivities of DAAs toward hydrocracking. Reactivities and reaction pathways of DAAs were found to depend not only on aromatic ring size, but also on the number of methylene between aromatic rings. Diarylmethanes were hydrocracked via C_{ar}–C_{alk} bond scission, while the C_{ar}–C_{alk} bond scission for 1,2-diarylethanes and 1,3-diarylpropanes seemed to be very difficult. These results could be interpreted by the hydrogen-accepting abilities of the ipso-carbons in the substrates and the resonance stabilities of the resulting arylalkyl radicals.

In general, coal liquefaction is considered to proceed through the cleavage of ether and methylene bridges connecting relatively small structure units, such as polycyclic aromatic, hydroaromatic, and naphthenic rings.[1—5] Particularly, the cleavage of relatively strong methylene bridges could be expected to play an important role in coal liquefaction.[6] Therefore, α,ω-diarylalkanes (DAAs) should be the most relevant model compounds for elucidating the mechanism of coal liquefaction.

So far, much effort has been directed to the elucidation of the mechanism for coal liquefaction by means of model reactions.[3,7—12] Most of the attention, however, was concentrated on the mechanistic clarification of the hydrogen-transfer process from solvents to coal or coal-related model compounds. Relatively few studies discussed the reaction mechanisms of DAAs at relatively low temperatures such as 300 °C, because of the ineffectiveness of hydrogen-donor solvents in the hydrogen-transfer process at the temperatures.[13] At high temperature, side reactions leading to the formation of light hydrocarbon gases (C_1—C_4) and coke become severe. Hence, in order to minimize the side reactions and to raise hydrogen utilization efficiency it is necessary to investigate the mechanisms of low-temperature coal liquefaction.

In recent years, several studies[14—19] have investigated on catalytic hydrogenation of coal at moderate temperatures. Prasad et al.[19] proposed that catalytic hydrogenation under mild conditions leads to the selective cleavage of methylene bridges. Skowronski et al.[16] carried out hydroliquefaction of bituminous coal in the temperature range of 275 to 325 °C. They concluded that high conversion to oil can be obtained at 325 °C with few side reactions resulting in gas or coke formation. Oil formation with high yield at moderate temperatures could be mainly ascribed to the use of an active catalyst. Therefore, catalytic hydrocracking at moderate temperatures should be a promising process for coal liquefaction.

Iron–sulfur systems are considered as effective catalysts for practical application because of their high catalytic activities for coal liquefaction and ready availabilities. Among the iron–sulfur systems, iron pyrite is a highly active catalyst. Its high catalytic activity was reported due to the formation of free radical intermediates such as H· and HS· caused by the pyrite–pyrrhotite transformation.[20—23] The pyrite–pyrrhotite transformation has been found to be possible[24—28] at temperatures significantly lower than those required for conventional coal liquefaction processes.

In this paper, DAAs were used as coal-related model compounds and their hydrocracking were studied using FeS_2 catalyst at 300 °C.

Experimental

Materials. Di-1-naphthylmethane (DNM) was synthesized according to the method described in an earlier paper,[29] and 1,2-di-1-naphthylethane (DNE) and 1,3-di-1-naphthylpropane (DNP) according to the method of Buu-Hoï[30] and Nishimura,[31] respectively. The other substrates such as biphenyl (BPh), 1,1′-binaphthyl (BNp), diphenylmethane (DPM), bibenzyl (BBz), 1,3-diphenylpropane (DPP), triphenylmethane (TPM) and the solvent decalin (DHN), were purchased commercially and further purified if necessary by conventional methods. Synthetic pyrite FeS_2 was offered by Asahi Chemical Industry Co., Ltd., which was preserved in a desiccator in which air was replaced with argon to prevent changes in chemical and physical properties.

Batch Experiments. A substrate (7.5 mmol), prescribed amounts of FeS_2 (0 g or 0.5 g) and 30 ml of DHN were put into a 90 ml stainless steel, magnetically stirred autoclave. In FeS_2-catalyzed reactions, 0.05 g of sulfur was added to the reaction systems to keep the catalytic activity of FeS_2.

After being pressurized by hydrogen to 10 MPa at room temperature (20 °C), the autoclave was heated up to 300 °C within 15 min and kept at the temperature for a prescribed period of time. Then the autoclave was immediately cooled to room temperature in an ice-water bath.

Product Analyses. The products were identified by GC-MS (Shimadzu GCMS QP-1000, equipped with a capillary glass column packed with Silicone OV-1, 0.24 mm in diameter and 50 m in length) if necessary and quantified by GC (Shimadzu GC-4CPTF, equipped with a stainless steel column packed with 5% Silicone OV-17 on Chromosorb WAW DMCS, 3 mm in diameter and 4.2 m in length). Bromobenzene was used as an internal standard for the quantification of the substrates and their reaction products.

Results

Noncatalytic Reactions. Hydrocracking reactions of BPh, BNp, TPM, and DAAs were performed under H_2 at 300 °C. In the absence of FeS_2 and sulfur, these reactions did not proceed at all even for 10 h. Namely, neither C–C bond scission nor hydrogenation of aromatic ring for the substrates used occurred under the reaction conditions. In the absence of FeS_2, sulfur addition promoted DNM hydrocracking to only a small extent (Table 1). The other substrates did not react at all with sulfur addition.

Hydrocracking of BPh, Diphenylalkanes (DPAs) and TPM. Table 2 summarizes the results of the hydrocracking of BPh, DPAs, and TPM with FeS_2. In order to compare the reactivities of these substrates distinctly, long-time (10 h) reactions were carried out for each substrate. BBz and DPP were not converted even after 10 h. The reaction of BPh only yielded cyclohexylbenzene via the hydrogenation of a benzene ring. Among the substrates, TPM showed the highest reactivity toward hydrocracking, affording benzene and DPM as major products together with small amount of toluene as a secondary product. Very small amount of hydrogenated product (cyclohexyldiphenylmethane) was observed. DPM hydrocracking also proceeded via the C_{ar}–C_{alk} bond scission, but DPM was much less reactive than TPM.

Hydrocracking of BNp and Dinaphthylalkanes (DNAs). The time profiles of the product distribution on FeS_2-catalyzed hydrocracking of DNM and DNE were shown in Figs. 1 and 2, respectively. DNM hydrocracking mainly produced naphthalene (NpH) and 1-methylnaphthalene (1-MN), via hydrogen addition to the ipso-position of DNM. Only small amount of hydrogenated di-1-naphthylmethanes (H-DNMs) was produced. As DNM hydrocracking proceeds, the selectivities of NpH and 1-MN decreased but those of tetralin (THN) and methyltetralins (MTs) increased, suggesting that NpH and 1-MN produced were hydrogenated to THN and MTs, respectively. DNM hydrocracking was much easier than DPM and TPM.

Drastically different from DNM, the reaction of DNE mainly yielded hydrogenated 1,2-di-1-naphthylethanes (H-DNEs) rather than decomposed products. The result shows that the cleavage of C_{ar}–C_{alk} linkage in DNE

Table 1. Additive Effect of Sulfur on DNM Hydrocracking[a]

Sulfur feed	DNM conv.	Selectivity/mol%		
g	%	NpH	1-MN	H-DNMs
0	0	—	—	—
0.05	0.7	80.6	100.0	Trace
0.32	3.4	98.6	99.5	0.5

a) DNM 7.5 mmol, decalin 30 ml, initial H_2 pressure 10 MPa, 300 °C, 1 h.

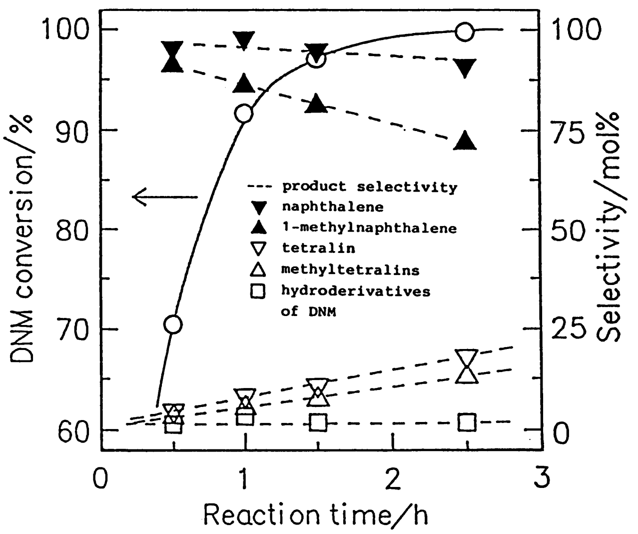

Fig. 1. Time profile of the product distribution in DNM hydrocracking catalyzed by FeS_2 at 300 °C. DNM 7.5 mmol, FeS_2 0.5 g, S 0.05 g, decalin 30 ml, initial H_2 pressure 10 MPa.

Table 2. FeS_2-Catalyzed Hydrocracking of BPh, DPAs, and TPM[a]

Substrate	Time	Conv.	Selectivity/mol%					
	h	%	PhH	PhMe	H-BPh	H-DPM	H-TPM	DPM
BPh	1	0.5	0	—	100.0	—	—	—
	10	6.2	0	—	100.0	—	—	—
DPM	1	3.1	100.0	100.0	—	0	—	—
	10	36.1	98.5	98.5	—	1.5	—	—
BBz	10	0	0	0	—	—	—	—
DPP	10	0	0	0	—	—	—	—
TPM	1	21.4	102.6	2.6	0	0	Trace	97.4
	10	87.7	118.5	20.4	—	0.5	0.5	79.5

a) Substrate 7.5 mmol, FeS_2 0.5 g, S 0.05 g, decalin 30 ml, initial H_2 pressure 10 MPa; PhH=benzene, PhMe=toluene; H-BPh, H-DPM, and H-TPM denote hydroderivatives of BPh, DPM, and TPM, respectively.

Table 3. FeS$_2$-Catalyzed Hydrocracking of BNp and DNAs[a)]

Substrate	Conv.	Selectivity/mol%									
	%	THN	NpH	MTs	1-MN	ETs	1-EN	PTs	1-PN	H-BNps	H-DNAs
BNp	11.4	22.3	17.3	—	—	—	—	—	—	43.3	—
DNM	91.7	4.3	95.7	3.6	89.0	—	—	—	—	—	2.9
DNE	50.7	0.2	1.8	2.7	2.3	0.3	0.4	—	—	—	86.8
DNP	51.1	1.5	10.3	0	Trace	0	Trace	4.9	7.0	—	88.1

a) Substrate 7.5 mmol, FeS$_2$ 0.5 g, S 0.05 g, decalin 30 ml, initial H$_2$ pressure 10 MPa; THN=tetralin, NpH=naphthalene, MTs=methyltetralins, 1-MN=methylnaphthalene, ETs=ethyltetralins, 1-EN=1-ethylnaphthalene, PTs=propyltetralins, 1-PN=1-propylnaphthalene; H-BNps and H-DNAs denote hydroderivatives of BNp and corresponding DNAs, respectively.

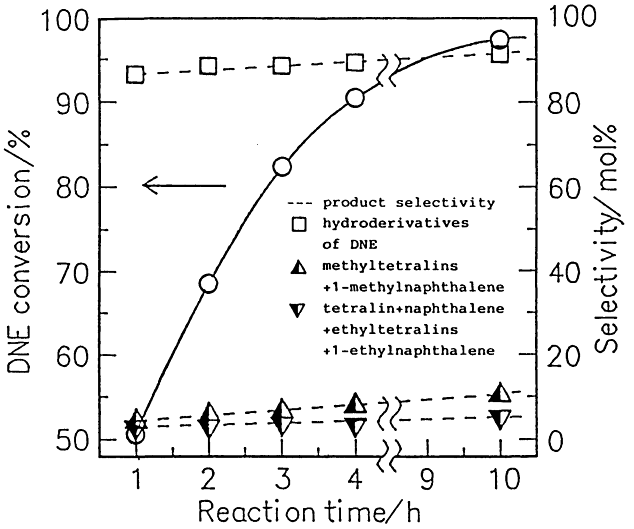

Fig. 2. Time profile of the product distribution in DNE hydrocracking catalyzed by FeS$_2$ at 300 °C. DNE 7.5 mmol, FeS$_2$ 0.5 g, S 0.05 g, decalin 30 ml, initial H$_2$ pressure 10 MPa.

is much more difficult than that in DNM. The total selectivity of 1-MN and MTs was higher than that of NpH, THN, 1-ethylnaphthalene (1-EN) and ethyltetralins (ETs), indicating FeS$_2$ accelerated C_{alk}–C_{alk} bond scission more than C_{ar}–C_{alk} bond scission in DNE hydrocracking.

Table 3 compares the results of the hydrocracking of BNp and DNAs. BNp hydrocracking afforded hydrogenated 1,1′-dinaphthyl (H-BNps) as main products. The total selectivity of decomposed products was higher than that in DNE hydrocracking. Similar conversion was observed in the reactions of DNE and DNP, but C_{ar}–C_{alk} bond scission in DNP seemed to be easier than that in DNE. DNP hydrocracking gave only traces of 1-MN and 1-EN, suggesting that C_{alk}–C_{alk} bond scission in DNP is difficult.

Discussion

Table 4 lists the C–H and C–C bond dissociation energies of some hydrocarbons. The central C–C bond in DNE is the weakest bond. The half-life of DNE for homolysis at 300 °C can be estimated according to that (14 h)[34)] of BBz for homolysis at 400 °C to be ca. 153 h. In the absence of catalyst, naphthalene conversion for hydrogenation at 400 °C was reported to be less than 1%.[37)] Hence, thermal reaction leading to hydrogenated or decomposed products is very difficult for any substrate used at 300 °C.

Table 4. Bond Dissociation Energies (BDE) of Some Hydrocarbons

Bond	BDE/kcal mol^{-1}	Reference
RCH$_2$-H	98±2	32
Ph-H	110	33
PhCH$_2$-H	85	33
Ph$_2$CH-H	83.8	34
Ph-Ph	113.7	34
PhCH$_2$-Ph	89.6	34
PhCH$_2$CH$_2$-Ph	99.9	34
PhCH$_2$-CH$_2$Ph	61.4	34
PhCH$_2$CH$_2$-CH$_2$Ph	73.9	34
NpCH$_2$-Np	85	35
NpCH$_2$CH$_2$-Np	97	36
NpCH$_2$-CH$_2$Np	55	36

R and Np denote straight-chain alkyl and 1-naphthyl group, respectively. 1 cal=4.184 J

Table 5. Resonance Energies (RE) of Some Benzylic Radicals

Radical	RE/kcal mol^{-1} [a)]
Benzyl	30.6
Diphenylmethyl	54.6
1-Naphthylmethyl	44.4

a) According to structure-resonance theory, see Ref. 38.

In general, C_{ar}–C_{alk} bond is very stable thermally. DPM hydrogenolysis does not proceed even at 430 °C.[29)] The results in Table 2 indicates that FeS$_2$ promoted the cleavage of C_{ar}–C_{alk} bond in TPM much more than that in DPM, but did not promote those in other substrates. Hydrogen atom addition to the ipso-position of an aromatic ring in the substrates is an essential step in C_{ar}–C_{alk} bond scission, especially at low temperature. But the ipso-addition of hydrogen atom does not necessarily result in C_{ar}–C_{alk} bond scission. The resonance stabilities of the resulting radicals could be also considered as an important factor. The data in Table 5 show the resonance energy of diphenylmethyl radical ($Ph_2CH\cdot$) is larger than that of benzyl radical ($PhCH_2\cdot$), suggesting that $Ph_2CH\cdot$ is produced more readily from TPM than $PhCH_2\cdot$ from DPM after the ipso-addition of hydrogen atom. Although no resonance energy data are available for phenyl, 2-phenylethyl and 3-phenylpropyl radicals, bond dissociation energies of C–H in Table 4 show that phenyl radical (Ph·) is much less stable than $PhCH_2\cdot$. The corresponding bond dissociation energies of $PhCH_2CH_2$–H and $PhCH_2CH_2CH_2$–H could be estimated to be approximately equal to that of RCH_2–H. 2-Phenylethyl and 3-phenylpropyl radicals are thereby considered to be a little more stable than Ph·, but much inferior to $PhCH_2\cdot$ in resonance energy. These data account for the difficulty in cleaving C–C bond in BPh, BBz, and DPP.

Superdelocalizability (S_r(R)) has been introduced to evaluate the reactivities of the unsaturated hydrocarbons toward radical reaction.[39] Futamura et al.[29] studied the hydrogenolysis of diarylmethanes. They reported that the relative reactivities of diarylmethanes toward hydrogenolysis can be interpreted on the basis of their different S_r(R) values. In other words, a carbon atom in an aromatic ring with larger S_r(R) value accepts hydrogen atom more readily.

BPh was more reactive toward hydrogenation than BBz and DPP, being related to its relatively higher hydrogen-accepting ability. The quantum chemical data in Table 6 indicate that the S_r(R) values of 2- and 4-positions in BPh are larger than that in benzene. The S_r(R) values of any position in BBz and DPP could be estimated not larger than that in benzene, since the data in Table 5 show that the S_r(R) value in an aromatic ring with alkyl or aromatic alkyl group is smaller than that without alkyl or aromatic alkyl group. Thus, BPh is more reactive toward hydrogenation than BBz and DPP.

The quite different reaction pathways of DNM and DNE may be explained by Fig. 3. The formation of 2-(1-naphthyl)ethyl radical ($NpCH_2CH_2\cdot$) is much more difficult than $NpCH_2\cdot$. Therefore, even though DNE accepts the ipso-addition of hydrogen atom to the same extent as DNM in FeS_2-catalyzed hydrocracking process, DNE decomposition to NpH and $NpCH_2CH_2\cdot$ induced by the ipso-addition of hydrogen atom is considered very difficult.

DNM was the most reactive toward hydrocracking. One reason for the high reactivity of DNM toward hydrocracking should be the large hydrogen-accepting ability of the ipso-carbon in DNM, which is quantitatively exhibited by S_r(R) value (Table 6). Another

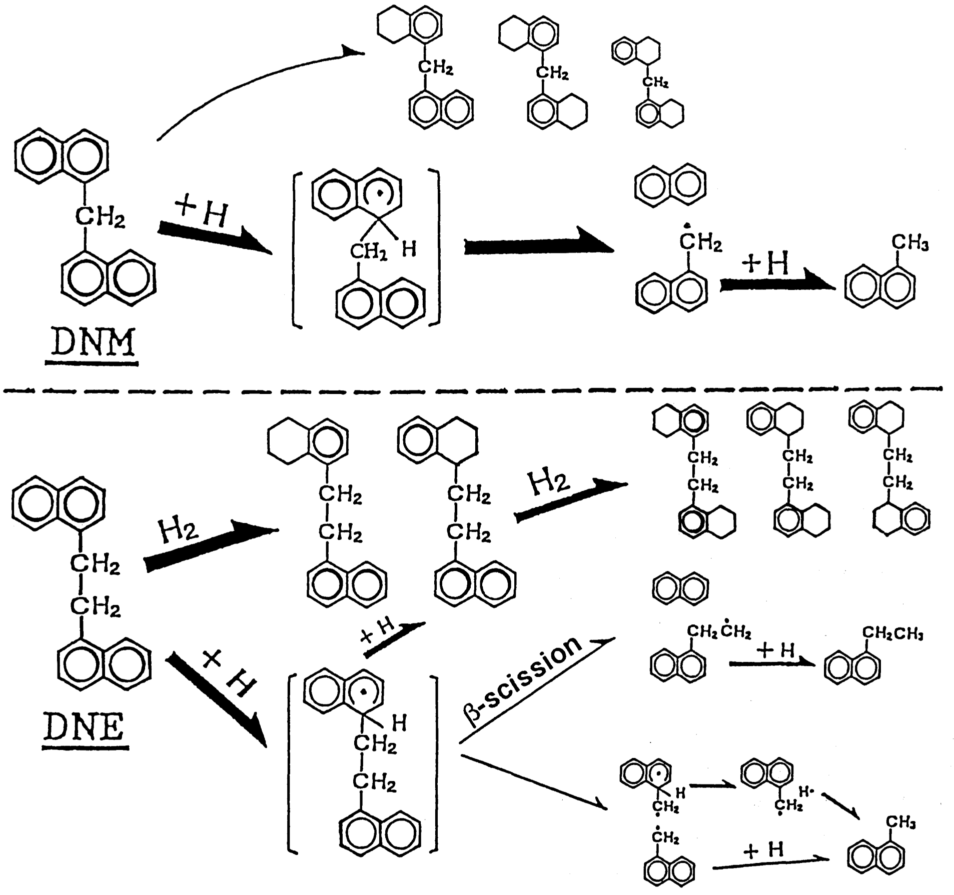

Fig. 3. Schemes for FeS_2-catalyzed hydrocracking of DNM and DNE.

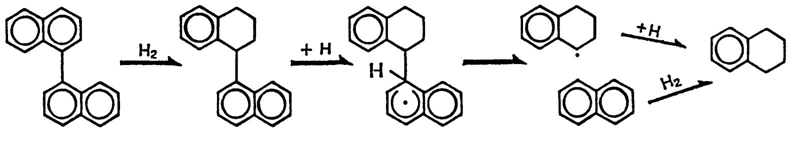

Fig. 4. Scheme for FeS_2-catalyzed hydrocracking of BNp.

Table 6. Superdelocalizability Values (S_r(R))[a] of Some Aromatic Hydrocarbons

Aromatic hydrocarbon	S_r(R) (position)	Reference
Benzene	0.8333	29
Biphenyl	0.7722(1-)	29
	0.910 (2-)	39
	0.830 (3-)	39
	0.894 (4-)	39
Diphenylmethane	0.8194(1-)	29
Naphthalene	0.9944(1-)	29
	0.873 (2-)	39
	0.703 (9-)	39
1-Methylnaphthalene	0.9770(1-)	29
1-Benzylnaphthalene	0.9773(1-)	29
Di-1-naphthylmethane	0.9773(1-)	29

a) Superdelocalizability values toward radical reaction.

reason should be the relatively high resonance stability of the resulting $NpCH_2\cdot$. The resonance energies in Table 5 suggest that $NpCH_2\cdot$ is much more stable than $PhCH_2\cdot$. The greatly higher reactivity of DNM than DPM toward hydrocracking should be due to the synergistic effect of the higher hydrogen-accepting ability of the ipso-carbon in DNM and the higher resonance stability of the resulting $NpCH_2\cdot$. Although $Ph_2CH\cdot$ is more stable than $NpCH_2\cdot$ according to the data in Table 5, TPM is less reactive than DNM because of its lower hydrogen-accepting ability.

C_{ar}–C_{ar} bond is stronger than C_{ar}–C_{alk} bond and its direct cleavage is very difficult even in the presence of FeS_2 because of the instability of the resulting aryl (phenyl or naphthyl) radical. Therefore, the decomposed products in BNp hydrocracking may be produced via the partial hydrogenation of a naphthyl-substituted benzene ring in 1,1′-binaphthyl, followed by hydrogen atom addition to the ipso-position of naphthalene ring in the resulting 1-naphthyltetralin (Fig. 4).

The difficulty of C_{alk}–C_{alk} bond scission in DNP hydrocracking compared to DNE hydrocracking may be due to the instablity of the resulting $NpCH_2CH_2\cdot$ from the cleavage of C_{alk}–C_{alk} linkage in DNP.

Conclusions

FeS_2 catalyst was found to be effective to catalyze the cleavage of C–C bridge in diarylmethanes, but at relatively low temperature, the catalyst plays only a small role in cleaving C–C bridges in α,ω-diarylalkanes with plural methylene linkages. These results suggest that at a low temperature selective cleavage of C–C bridge could take place in FeS_2-catalyzed coal liquefaction.

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