FeS_2-Catalyzed Hydrocracking of Di(1-naphthyl)methane. Efffects of Hydrogen Pressure, Catalyst Feed and Reaction Temperature, and Kinetic Study

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Hydrocracking of di(1-naphthyl)methane (DNM) in the temperature range of 150—300 °C was studied. In the presence of FeS_2 and pressurized hydrogen, DNM hydrocracking took place over 175 °C. FeS_2 selectively catalyzed the cleavage of C–C linkage in DNM to give 1-methylnaphthalene and naphthalene. The rate for DNM hydrocracking strongly depended on hydrogen pressure, FeS_2 feed and reaction temperature. Kinetic study indicates that DNM hydrocracking in the temperature range of 200—300 °C could be considered as a first order reaction. Under the reaction condition (DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, sulfur 0.05 g, initial hydrogen pressure 10 MPa), the activation energy and frequency factor for DNM hydrocracking were 19 kcal mol^{-1} and 5.3×10^{7} h^{-1}, respectively.

The cleavage of C–C linkage in coal structure is one of the most important reactions in coal liquefaction.[1] A number of workers have investigated the effects of molecular hydrogen,[2] hydrogen sulfide,[2,3] solvents,[4,5] and catalyst[1–3,6] on the cleavage of C–C linkage in coal-related model compounds. In general, C_{ar}–C_{alk} bond cleavage is thermally much more difficult than C_{alk}–C_{alk} bond cleavage, but in the presence of a proper catalyst, C_{ar}–C_{alk} bond can be selectively cleaved even at a lower temperature.

Farcasiu and Smith[6] studied carbon black-catalyzed decomposition of 4-(1-naphthylmethyl)bibenzyl (**1**). Their results indicate that in the presence of carbon black the cleavage of the bond between naphthyl unit and methylene linkage in **1** takes place at temperatures as low as 320 °C. But **1** conversion is less than 4% at 320 °C. In a recent paper,[7] we reported that in the presence of FeS_2 the hydrocracking of di(1-naphthyl)-methane (DNM) proceeded rapidly at 300 °C. This result implies that FeS_2-catalyzed hydrocracking of DNM may proceed even at the temperatures lower than 300 °C.

It is well known that raising reaction temperature to increase the rate of oil formation not only consumes more energy to keep the elevated temperature but also results in an increase in the yield of light hydrocarbon gases (C_1—C_4), leading to even poorer hydrogen efficiency.[8–11] Therefore, catalytic coal liquefaction at low temperature should be noteworthy.

This paper examines the effects of hydrogen pressure, FeS_2 feed and reaction temperature, and reports kinetic study on FeS_2-catalyzed hydrocracking of DNM in the temperature range of 200—300 °C.

Experimental

Materials. DNM was synthesized by heating naphthalene (NpH) with 1-chloromethylnaphthalene in the presence of zinc power.[12] Decalin used as solvent was commercial reagent and used without further purification. Synthetic pyrite FeS_2 was offered by Asahi Chemical Industry Co., Ltd.

Procedure. DNM (7.5 mmol), prescribed amount (0—0.5 g) of FeS_2, 0.05 g of sulfur, and 30 ml of decalin were put into a 90 ml stainless steel, magnetically stirred autoclave. After being pressurized with hydrogen to a desired pressure (0—10 MPa) at room temperature (20 °C), the autoclave was heated to a reaction temperature (150—300 °C) within 15 min and maintained for a prescribed time (0.5—10 h). Then, the autoclave was immediately cooled to room temperature in an ice-water bath.

Analyses. The products were identified by GC–MS (Shimadzu GCMS QP-1000, equipped with a glass capillary column of 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 column of 5% Silicone OV-17 on Chromosorb WAW DMCS, 3 mm in diameter and 4.2 m in length).

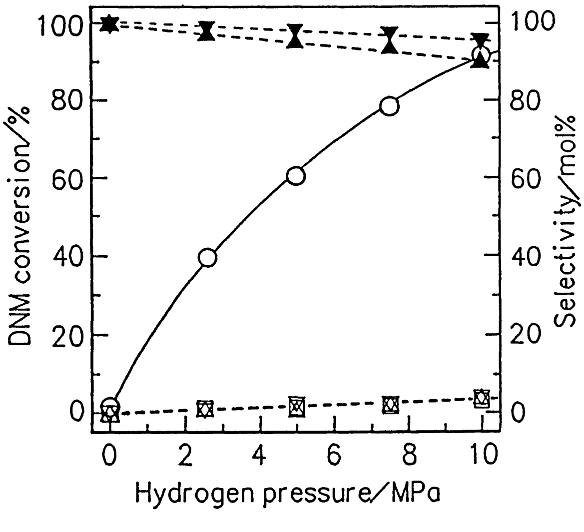

Fig. 1. Effect of initial hydrogen pressure on DNM hydrocracking.
DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, S 0.05 g, 300 °C, 1 h; ▼ naphthalene, ▲ 1-methylnaphthalene, ▽ tetralin, △ methyltetralins, □ hydrogenated di(1-naphthyl)methanes.

Results and Discussion

Effect of Hydrogen Pressure. Figure 1 illustrates the effect of initial hydrogen pressure on DNM hydrocracking in the presence of FeS_2 at 300 °C. Under nitrogen, DNM conversion was ca. 1.4%, suggesting that hydrogen transfer from decalin to DNM occurred to only a small extent. Similar to the results of DNM hydrocracking at 430 °C,[13] increasing hydrogen pressure greatly enhanced DNM conversion. The total selectivity of hydrogenated di(1-naphthyl)methanes (H-DNMs) increased with increasing hydrogen pressure but was less than 3%. This result indicates that although increasing hydrogen pressure enhanced probability for naphthalene rings in DNM to be hydrogenated to some extent, FeS_2 mainly catalyzed the cleavage of C–C linkage in DNM rather than the hydrogenation of naphthalene rings in DNM. The selectivities of the secondary products such as tetralin (THN) and methyltetralins (MTs) were also increased to some extent by increasing initial hydrogen pressure.

Effect of FeS_2 Feed. Table 1 shows the effect of FeS_2 feed on DNM hydrocracking at 300 °C. In the absence of FeS_2 and sulfur, DNM hydrocracking did not proceed at all. Sulfur addition promoted DNM hydrocracking to very small extent (DNM conversion$<$ 1%). DNM conversion increased remarkably with increasing FeS_2 feed. No significant change in product distribution was observed.

Elemental sulfur has been reported to produce significant amount of active radicals$>$180 °C,[14] but the results in Table 1 indicate that at low temperature (300 °C) the resulting active radicals did not induce the cleavage of C–C linkage in DNM sufficiently and that DNM hydrocracking proceeded on the surface of iron sulfides. No appreciable amount of sulfur-containing aromatic products was observed, suggesting that H-atoms rather than active sulfur radicals directly induced DNM hydrocracking. Active sulfur radicals, especially pyritic sulfur radicals may indirectly induce DNM hydrocracking via producing active hydrogen atoms.[15]

Effect of Reaction Temperature. Table 2 lists the results of DNM hydrocracking in the temperature range of 150—300 °C. DNM hydrocracking failed to proceed at 150 °C. At 175 °C, only 0.3% of DNM was hydrocracked to naphthalene (NpH) and 1-methylnaphthalene (1-MN). Raising reaction temperature remarkably accelarated DNM hydrocracking. The selectivities of tetralin (THN) and methyltetralins (MTs) increased with raising reaction temperature.

At temperatures higher than 130 °C hydrogen abstraction induced by the ring scission of elemental sulfur may occur,[13] producing free H-atoms. But in the case of the reaction at 150 °C it is not clear:
1) whether the resulting H-atoms can attack naphthalene rings in DNM (step 1);
2) even though H-atom addition to naphthalene rings takes place, as step 2 whether the resulting cyclohexadienyl radicals can accept one or more H-atoms to produce H-DNMs (for non-ipso-substituted cyclohexadienyl radicals), or undergo β-scission to give NpH and 1-MN (for ipso-substituted cyclohexadienyl radical).
Because DNM was not converted at all at 150 °C, it can be said that at least one of the two reactions (steps 1 and 2) did not occur at such a low temperature.

Table 1. Effect of FeS_2 Feed on DNM Hydrocracking[a]

FeS_2 feed	DNM conv.	Selectivity/mol%				
mg	%	THN	NpH	MTs	1-MN	H-DNMs
0[b]	0	—	—	—	—	—
0	0.7	—	80.6	0	100	trace
125	37.1	2.1	98.7	1.9	94.5	2.1
250	53.3	2.8	99.4	2.5	90.7	2.3
375	89.0	2.2	99.9	2.2	92.5	1.5
500	91.7	4.3	95.7	3.6	89.0	2.9

a) DNM 7.5 mmol, decalin 30 ml, S 0.05 g, initial H_2 pressure 10 MPa, 300 °C, 1 h. b) Without sulfur addition; THN: tetralin, NpH: naphthalene, MTs: methyltetralins, 1-MN: 1-methylnaphthalene, H-DNMs: hydrogenated di(1-naphthyl)methanes.

Table 2. Effect of Reaction Temperature on DNM Hydrocracking[a]

Temp	Conv.	Selectivity/mol%				
°C	%	THN	NpH	MTs	1-MN	H-DNMs
150	0	—	—	—	—	—
175	0.3	0	100	0	100	0
200	9.2	Trace	98.6	Trace	98.4	1.5
225	22.6	1.6	99.4	0.5	94.6	1.7
250	44.5	3.9	94.2	1.8	95.0	1.9
300	91.7	4.3	95.7	3.6	89.0	2.9

a) DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, S 0.05 g, initial H_2 pressure 10 MPa, 1 h.

Table 3. Time Profile of DNM Conversion[a]

Temp/ °C	Time/h	Conv./%
200	1.0	9.7
	3.0	21.9
	6.0	39.5
	10.0	55.1
225	1.0	22.6
	3.0	59.5
	6.0	78.5
	10.0	90.4
250	1.0	44.5
	2.0	64.0
	3.0	80.0
	5.0	92.2
	8.0	98.3
300	0.5	70.1
	1.0	91.7
	1.5	97.1
	2.5	99.6

a) DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, S 0.05 g, initial H_2 pressure 10 MPa.

Kinetics of FeS_2-Catalyzed Hydrocracking of DNM. As discussed above, DNM hydrocracking strongly depended on hydrogen pressure, FeS_2 feed and reaction temperature. In the presence of FeS_2, DNM was selectively hydrocracked to NpH and 1-MN.

If neglecting H-DNMs formation, DNM hydrocracking may be approximately considered as a first order reaction. The relation between DNM conversion X and reaction time t can be written as follows:

$$\ln(1-X)^{-1}=kt,$$

where k denotes the pseudo-first-order rate constant.

Table 3 demonstrates the data of reaction time and DNM conversion in the temperature range of 200—300 °C. The corresponding plots of $\ln(1-X)^{-1}$ versus reaction time were shown in Fig. 2. Good linear correlations suggest that the consideration of DNM hydrocracking being a pseudo-first-order reaction is appropriate.

The pseudo-first-order rate constants were calculated from the slope of plots of $\ln(1-X)^{-1}$ versus reaction time for each reaction temperature and listed in Table 4. Using the data in Table 4 an Arrhenius plot was obtained (Fig. 3), which also exhibits a good linear correlation. The activation energy and frequency factor calculated from the slope of $\ln k$ versus T^{-1} plot (Fig. 3) are 19 kcal mol^{-1} and 5.3×10^{7} h^{-1}, respectively.

The same activation energy was reported for the cleavage of the bond between naphthyl unit and methylene linkage in model compound **1** in the presence of 5 wt% of carbon black based on **1** in the temperature range of 360—429 °C.[6] Because of the different substrates and reaction conditions, it is difficult to compare the activities and selectivities of FeS_2 and carbon black (Black Pearls 2000) for C_{ar}–C_{alk} bond scission according to the data in this paper and those published by Farcasiu and Smith.[6] But FeS_2 may be more worth noting because it selectively catalyzed the cleavage of C–C linkage in DNM at temperatures as low as 175 °C.

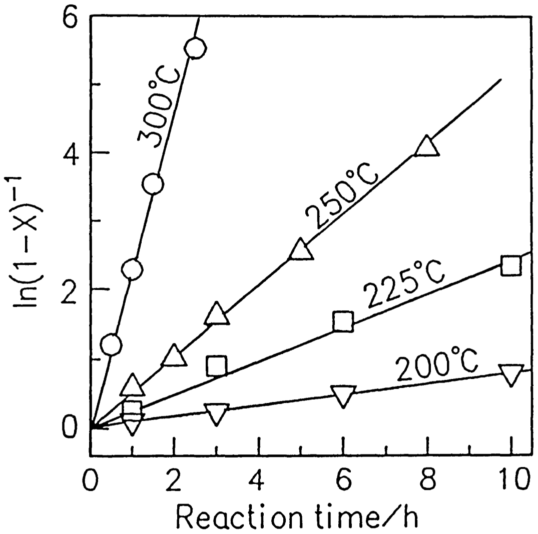

Fig. 2. Kinetics of DNM hydrocracking.
DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, S 0.05 g, initial H_2 pressure 10 MPa.

Table 4. Pseudo-First-Order Rate Constants for DNM Hydrocracking[a)]

Temp/ °C	k/h^{-1}
200	8.1×10^{-2}
225	24.1×10^{-2}
250	53.0×10^{-2}
300	280.0×10^{-2}

a) DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, S 0.05 g, initial H_2 pressure 10 MPa.

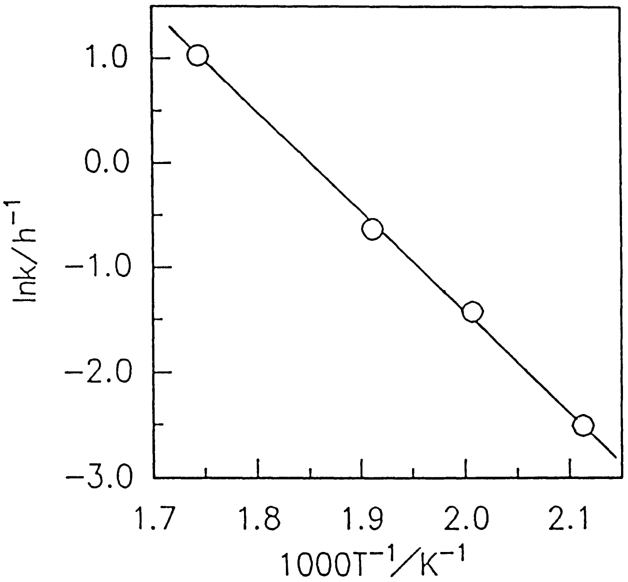

Fig. 3. Arrhenius plot for DNM hydrocracking.
DNM 7.5 mmol, decalin 30 ml, FeS_2 0.5 g, S 0.05 g, initial H_2 pressure 10 MPa.

Studies on the reactivities of other coal-related model compounds and the activities of other catalysts at low temperatures are in progress. If Black Pearls 2000 and model compound **1** are available, we will compare the activities and selectivities of FeS_2 and Black Pearls 2000 for the hydrocracking of DNM and **1** and examine the catalytic mechanisms of both catalysts in detail.

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