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Catalyses of Fe and FeS_2 on the Reaction of Di(1-naphthyl)methane

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Reactions of di(1-naphthyl)methane (DNM) over Fe and FeS_2 at 300 °C were carried out to investigate the catalytic activities and selectivities of the two catalysts. Both catalysts showed high activities for the reaction of DNM but Fe catalyzed DNM hydrogenation whereas FeS_2 catalyzed DNM hydrocracking. This difference can be ascribed to the presence of sulfur.

Compared to the conventional coal liquefaction processes performed at high temperature, low-temperature coal liquefaction may be more promising in view of the fact that the formation of gaseous products and coke can be considerably reduced at low temperature. Active catalyst is necessary to accelarate oil formation. Iron-sulfur systems are considered as effective catalysts for practical application because of their high catalytic activities for coal liquefaction and ready availabilities. In this paper, we used DNM as a coal-related model compound and examined the catalytic effects of Fe and FeS_2 on the reactions of DNM.

DNM was synthesized according to the method described in an earlier paper.[1)] 1-Methylnaphthalene (1-MN), decalin, sulfur and catalyst Fe (ultra fine particles of Fe) were purchased commercially. Synthetic pyrite FeS_2 was offered by Asahi Chemical Industry Co. Ltd.

Prescribed amount of a substrate (DNM or 1-MN), sulfur, 4.2 mmol of a catalyst and 30 ml of decalin were put into a 90 ml stainless steel, magnetically stirred autoclave. After being pressurized by hydrogen or nitrogen 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 1 h. Then the autoclave was immediately cooled to room temperature in an ice-water bath. Reaction products were identified by GC-MS if necessary and quantified by GC.

Table 1 lists the results of non-catalytic and catalytic reactions of DNM. In the absence of catalyst, DNM was not converted at all even under pressurized hydrogen. Only small amount of DNM was converted in the pre-

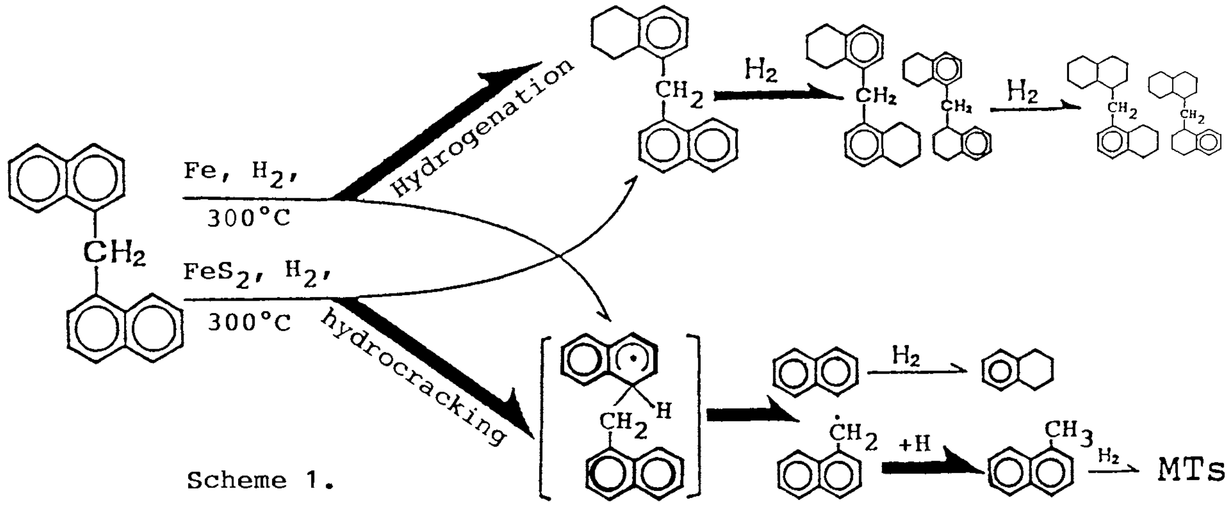
Table 1. Catalytic effects of Fe and FeS_2 on DNM hydrocracking[a)]

Catalyst	Gas phase	DNM conv.	Selectivity / mol%				
		%	THN	NpH	MTs	1-MN	H-DNMs
None	H_2	0	0	0	0	0	0
FeS_2[b)]	N_2	1.4	-	-	0	100.0	0
Fe	H_2	100.0	1.0	0	0.8	0	99.0
FeS_2[b)]	H_2	91.7	4.3	95.7	3.6	89.0	2.9

a) DNM 7.5 mmol, catalyst 4.2 mmol, decalin 30 ml, initial H_2 or N_2 pressure 10 MPa, 300 °C, 1 h; b) with 1.6 mmol of sulfur addition;
THN: tetralin, NpH: naphthalene, MTs: methyltetralins,
1-MN: 1-methylnaphthalene, H-DNMs: hydrogenated di(1-naphthyl)methanes.

sence of FeS_2 under pressurized nitrogen. DNM conversion was more than 90% in the presence of Fe or FeS_2 under pressurized hydrogen. These results suggest that catalyst and molecular hydrogen play significant roles in the reaction of DNM. In Fe-catalyzed reaction, DNM was completely converted, affording hydrogenated di(1-naphthyl)methanes (H-DNMs) as main products with 99% of total selectivity. 91.7% of DNM was converted in the reaction catalyzed by FeS_2, which was quite different from Fe-catalyzed reaction, overwhelmingly major products were decomposed products such as naphthalene (NpH) and 1-MN, while only a small amount of H-DNMs with less than 3% of total selectivity was observed.

Scheme 1 illustrates the reaction pathways of DNM with Fe and FeS_2. It is evident that under the reaction condition, Fe catalyzed the hydrogena-



Scheme 1.

tion of naphthalene rings in DNM whereas FeS_2 catalyzed the cleavage of C-C bond in DNM. Based on the suggestion2) that the hydrogen trasfer to the non-ipso positions of DNM does not lead to C-C bond cleavage, Fe is considered to selectively promote the hydrogen transfer to the non-ipso positions of DNM, while selective hydrogen tranfer occurs to ipso-position of DNM in FeS_2-catalyzed reaction.

Figure 1 demonstrates the additive effect of sulfur on Fe-catalyzed reaction of DNM. DNM conversion falled rapidly with sulfur addition until S/Fe = 0.04, but increased with increasing sulfur feed afterwards. On the other hand, the selectivity of H-DNMs decreased monotonously with the increase of sulfur feed. These facts indicate evidently that sulfur added inhibited DNM hydrogenation, but promoted the cleavage of C-C linkage in DNM during the reactions. It is reasonable that the significant difference in selectivities between Fe and sulfur-containing species such as iron sulfides and H_2S resulted in the changes in reactivity and reaction pathway for the reaction of DNM.

Furthermore, we studied the additive effect of sulfur on 1-MN hydrogenation. As Fig. 2 shows, similar change in conversion for 1-MN hydrogenation was observed compared to DNM hydrogenation/hydrocracking (Fig. 1). 1-MN was hydrogenated to methyltetralins (MTs), i.e., 1-methyltetralin (1-MT) and 5-methyltetralin (5-MT). Increasing sulfur feed increased [1-MT]/[MTs] ratio, suggesting that sulfur addition enhanced probability

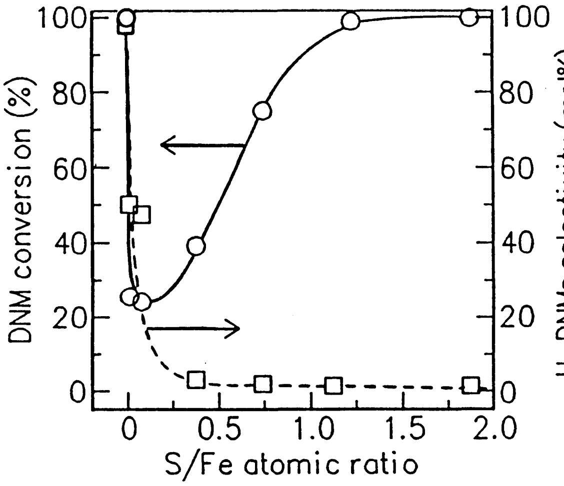


Fig. 1. Additive effect of sulfur on DNM hydrogenation/hydrocracking. DNM 7.5 mmol, Fe 4.2 mmol, decalin 30 ml, initial H_2 pressure 10 MPa, 300 °C, 1 h.

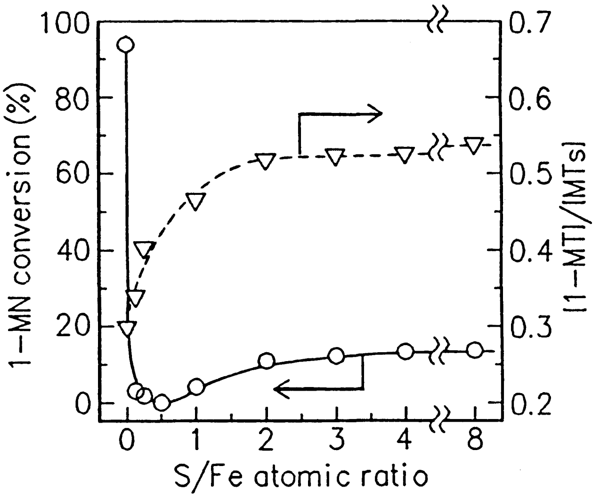
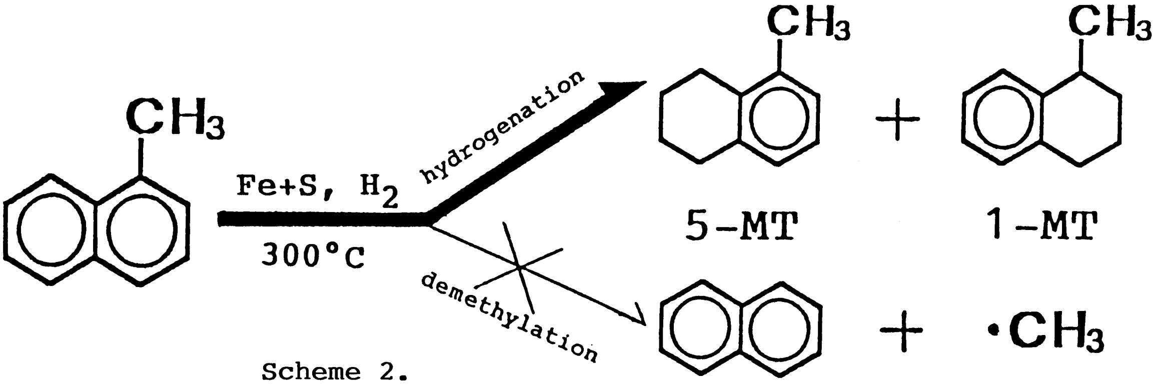


Fig. 2. Additive effect of sulfur on 1-MN hydrogenation. 1-MN 15 ml, Fe 4.2 ml, decalin 30 ml, initial H_2 pressure 10 MPa, 300 °C, 1 h.

for methyl-substituted moiety of 1-MN to be hydrogenated. It is noteworthy that when S/Fe atomic ratio was 2, futher increase of sulfur feed hardly affected either 1-MN conversion or [1-MT]/[MTs] ratio. The cleavage of C-C bond between methyl group and naphthalene ring affording NpH and tetralin can not occur under the reaction condition (Scheme 2), since methyl radical is much less stable than naphthyl-1-methyl radical. Therefore, it is not clear whether the hydrogenation of methyl-substituted moiety in 1-MN occurred preferentially via hydrogen addition to the ipso-position of 1-MN.



Scheme 2.

The above findings may be helpful in understanding the additive effect of sulfur on coal liquefaction under mild condition. Fe was shown to be an excellent catalyst for the hydrogenation of DNM and 1-MN, but exhaustive desulfurization should be necessary for coal hydrogenation, since even a small amount of sulfur present in coal may decrease the activity of Fe for hydrogenation reaction. Taking into account the fact that C_{ar}-C_{alk} bond scission is very difficult in thermal reaction,[3] FeS_2 is worth noting because it selectively and effectively promotes the cleavage of C_{ar}-C_{alk} bond in DNM at the temperature significantly lower than that required for conventional coal liquefaction. FeS_2 has been suggested to facilitate the formation of free radical intermediates such as H• and •HS,[4-5] whereas Fe-catalyzed hydrogenation of DNM and 1-MN may not involve free radical process.

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