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Catalysis of iron sulfates on hydroconversion of 1-methylnaphthalene

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Abstract

In order to develop suitable catalyst for hydroconversion of heavy hydrocarbon materials, possibility of high quality catalyst production from iron sulfates was pursued on the hydroconversion of 1-methylnaphthalene (1-MN). Catalytic activities of iron sulfates were very low in the absence of sulfur (S). Hydrogenation activity of ferrous sulfate dramatically increased with addition of S. Activity of ferric sulfate, however, did not increase with addition of S. From XRD analysis of catalysts recovered after the reaction, it indicated that ferrous sulfate was transformed to pyrrhotites $Fe_{1-x}S$ above 350°C in the presence of enough S. But ferric sulfate was not transformed to pyrrhotites easily. Effect of reaction temperature and additive effects of S, presulfiding temperature and sulfuric acid to the activity, selectivity and structure of iron sulfates were investigated in detail. From results of 1-MN hydroconversion, ferrous sulfate is revealed one of useful catalyst precursors for hydrogenation of aromatic hydrocarbon. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Iron sulfates catalyst; Hydroconversion; 1-methylnaphthalene; Sulfiding of iron sulfates

1. Introduction

The molecular weight of utilizable fossil resources will become heavier and heavier with the passage of time. Hydroconversion for the production of lower materials and hydrogen-rich clean derivatives is a important method in the utilization of heavy hydrocarbon resources which include a lot of hetero atoms and mineral matters. The catalyst will be quickly deactivated by deposition and adhesion of mineral matter and coke during long time of these hydrotreatment.

Utilization processes of heavy fossil hydrocarbon have to be considered in a worldwide scale. Catalyst for the utilization needs to equip next points: high activity, suitable selectivity, low price, a lot of available resources and wide distribution in the world. All price is always decided by relationship of demand and supply. The prices will be quickly jumped up to high level a lot of the consumption of small amounts rescouses element such as molybdenum, tungsten, nickel, cobalt and precious metals. We already had experiences of two oil shocks in 1973 and 1979 resulting in a little unbalance of demand and supply

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of oil. Iron is one transition metal conformed to satisfy these needs. Iron is low in price, a lot of resources and in wide distribution throughout the world.

In investigations of catalysis of pyrite (FeS_2), we recently proved that fine pyrite powder was oxidized to iron sulfates in a part under air storage and the catalytic activities of pyrite to the hydrogenation and hydrocracking of polycyclic aromatics and arylalkanes were decreased by the oxidation of iron sulfide catalyst [1,2]. The deactivated iron sulfide catalysts were reactivated by using excess S to higher levels than that of original pyrite. Hirano and co-worker recently reported similar results of catalytic activity on the coal liquefaction in the case of natural pyrite [3,4]. It is worth noting that catalysis of iron sulfates in the hydroconversion of 1-MN is interested in the development of high quality catalysts for hydroconversion of heavy hydrocarbon materials as a basic study. Catalysts used in such conversion processes will be rapidly fouled or deactivated by the deposition of a lot of carbonaceous materials and mineral matters contained onto the catalyst surfaces.

It is well known that one of the solutions of such problems is the use of highly active and low priced disposable catalysts. Pruden and co-worker reported a slurry upgrading process of heavy residues in the presence of iron sulfate catalyst [5]. But the catalysis of iron sulfates did not clear in detail. Many processes were already proposed for using oil soluble transition metal compounds for hydrocracking and upgrading of heavy oil [6]. Ozaki recently reviewed the upgrading of residual oils in detail [7]. It was reported very recently that ferrous sulfate ($FeSO_4{\cdot}7H_2O$) [8] and ferric oxyhydroxysulfate ($Fe_8O_8(OH)_8SO_4$) [9] in the presence of S are active in the hydrocracking of 4-(1-naphthylmethyl)bibenzyl. We took notice of iron sulfates catalyst because the iron sulfates were easily produced by the reaction between sulfuric acid and many kinds of iron resources, such as iron ores, scraps and waste recycle materials containing iron.

On the other hand, direct and indirect liquefactions of coal which is one of the fouling heavy carbonaceous resources have been performed by using many ideas and methods. Uses of many types of catalysts are continuing from the 1900s to the present time on various scales from laboratory scales to large plants by a number of workers. For example, coal liquefaction is very accelerated by the coal impregnation of iron sulfate aqueous solution [10,11] and the catalytic activity of iron oxide is increased by using characteristic addition of sulfate anion [12]. In Japan, a coal liquefaction study with a pilot plant of 150 t/d scale, named ‘NEDOL process’ was started from 1996. The process probably uses iron sulfide catalysts.

We recently reported hydroconversion in the presence of metallic iron and some iron sulfides catalysts [13–15]. The pyrite as one iron catalyst precursor selectively promoted C_{ar}–C_{alk} bond cleavage of diarylmethanes with hydrogen-atom insertion to *ipso*-carbon in the aromatic-rings of substrate molecules. But in the case of diaryl, diarylethanes and diarylpropanes, the pyrite promoted hydrogenation of the aromatic-rings without C–C bond breaking. In this paper, catalytic activity and selectivity and structure of ferrous sulfate and ferric sulfate were evaluated during the hydroconversion of 1-MN in the presence and absence of various amount of S.

2. Experimental

2.1. Materials

Decalin (DHN) and 1-MN and were used after elimination of impurities by passing through a column packed with a lot of activated alumina. Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and ferric sulfate ($Fe_2(SO_4)_3{\cdot}nH_2O$) for catalysts and catalyst precursors and elemental solid sulfur (S) were commercial reagents and were used without further treatment or purification, unless otherwise noted.

2.2. Batch reaction conditions

We adopted two reaction methods. In one typical reaction, 1.0 g (7.1 mmol) of 1-MN, iron sulfate (Fe 2.2 mg-atom) and S (6.0 mg-atom) and 30 ml (191 mmol) of DHN were put into a 150 ml stainless steel (SUS 316), magnetically-stirred autoclave (Nitto Koatsu Inc. Co.). The reactor was purged three times with hydrogen (H_2) of over 10 MPa and then pressurized with H_2 to 10 MPa at room temperature. The autoclave was heated up to the prescribed temperature (usually 350°C) within 20 min and kept at the temperature for 1 h. After the reaction, the hot reactor was immediately quenched in an ice-water bath. During heating of the autoclave the substrates in the autoclave were stirred by two blades magnetically induced at 1000 rpm to provide mixing and hydrogen dissolution. Another method is the hydroconversion with presufided catalysts at several temperatures before the 1-MN hydroconversion reaction. That is at first iron sulfate and S, 30 ml of DHN and 10 MPa of H_2 were introduced the autoclave and the iron sulfate was sulfided at several temperatures. After the gaseous materials in autoclave were liberated at room temperature, 1-MN and S and 10 MPa of H_2 were put into the autoclave. Then 1-MN hydroconversion was carried out by heating at 350°C for 1 h.

2.3. Products analyses

The liquid products were identified by gas chromatography/mass spectrometry (GC–MS) using a Shimadzu GC–MS Model QP-1000 coupled with a mass selective detector operating in the electron-impact mode at 70 eV and combined with a computer system Shimadzu GC-MSPAC-200, equipped with a capillary glass column chemical-bonded with Silicone grease OV-1, 0.24 mm in diameter and 60 m in length. The products were quantified by two different detectors and two columns: a flame ionization detector of gas chromatography Shimadzu Model GC-15A equipped with the same column of GC–MS and thermal conductivity detectors of gas chromatography GC-9A equipped with two packed stainless steel columns of 3 mm in diameter and 5 m in length with 5 wt.% Silicone grease OV-1 on Chromosorb W treated with AW-DMCS method. The GC quantitative data were calculated by using Shimadzu Chromatopac C-R4A installed along with the GC system with using of an internal standard method. Original, pretreated and recovered iron catalysts after the reaction were analyzed by means of XRD method (Rigaku Denki, Model RINT 2400), using X-ray of Cu K_α line at 40 kV and 200 mA.

3. Results and discussion

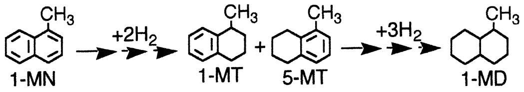
3.1. Additive effects of S for catalysis of ferrous sulfate

Table 1 shows the results of typical additive effects of S (S/Fe atomic ratio=2.5) to the hydroconversion of 1-MN in the presence of ferrous sulfates catalysts roughly grinned or not grinned with a ceramics mortar at 350°C for 1 h. Original ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and its dried sulfates had a low activity for 1-MN hydroconversion in the absence of S. Hydrogenation activity of ferrous sulfates, however, was increased dramatically with addition of S (S/Fe atomic ratio=2.5). Added S was apparently in stoichiometrical excess of amounts needed for formation of troilite (FeS), pyrrhotites ($Fe_{1-x}S$) and pyrite (FeS_2), but not enough to form pyrite from the phase diagram of $Fe–H_2–H_2S$ system [16–18].

Table 1
Hydroconversion of 1-methylnaphthalene with ferrous sulfate catalysts at 350°C for 1 h

Catalyst[a]	Grind[b]	Dry[c]	S-add.[d]	Structure[e]	Conv. (%)[f]	4H-select. (%)[g]	5-MT/1-MT[h]
$FeSO_4{\cdot}7H_2O$	Yes	No	No	$FeSO_4{\cdot}7H_2O$	1.4	—	—
	Yes	Yes	No	$FeSO_4{\cdot}H_2O$	2.0	~20	—
	No	No	Yes	$FeSO_4{\cdot}7H_2O$	36.0	86	1.11
	Yes	No	Yes	$FeSO_4{\cdot}7H_2O$	43.5	84	1.10
	Yes	Yes	Yes	$FeSO_4{\cdot}H_2O$	42.5	90	1.11

[a] Using of 2.2 Fe g-atom catalyst.
[b] Grinding of iron sulfate.
[c] Drying at 150°C fro 10 h before the reaction.
[d] Sulfur addition as S/Fe atomic ratio=2.5.
[e] Main structure of catalyst before starting the reaction.
[f] Conversion of 1-methylnaphthalene.
[g] Selectivity of methyltetralins.
[h] Ratio of 5-methyltetralin/1-methyltetralin.



(1)

Hydrogenation of 1-MN will be proceed as in Eq. (1). Major products from 1-MN hydroconversion with ferrous sulfate catalyst in the presence of enough S were 1-methyltetralin (1-MT) and 5-methyltetralin (5-MT). 1-Methyldecalins (1-MDs) as the completely hydrogenated derivatives of the aromatic-rings in 1-MN molecules were also determined a little. Ratios of 5-MT/1-MT in the products were always about 1.1 in the presence of enough S. It suggests that the hydrogenation of aromatic-ring bonded with methyl-group in 1-MN molecule is only a little difficult to compare with the hydrogenation of the non-methylated-ring.

3.2. *Additive effects of S for catalysis of ferric sulfate*

Hydroconversion of 1-MN with ferric sulfates catalyst in the absence and additive effects of S to hydroconversion of 1-MN with ferric sulfate catalyst are shown in Table 2. Conversions of 1-MN with ferric sulfates in the absence of S were low level between 6% and 7%. These conversions were a little higher than those in the case of ferrous sulfates. Selectivities of 1-MT and 5-MT as tetrahydro-derivatives of 1-MN were very low in the case of ferrous sulfates in the absence of S. The conversion of 1-MN did not increase by S addition when the S/Fe atomic ratio is 2.5. The major product was naphthalene and a very little tetralin was produced. In order to low 1-MN conversion, distinction of naphthalene and tetralin formations difficult from 1-MN with demethylation or from dehydrogenation of decalin. All recovered liquids after the 1-MN reaction in the presence of ferric sulfates catalysts were light yellow. Small peaks over 20 were observed in a gas chromatogram of the products with ferric sulfate catalyst. But we could not clearly assigned characteristic compound by GC–MS analysis in order to a little of each fraction. These results indicate that some complicated reactions occurred.

3.3. *Effects of reaction temperature on the 1-MN hydroconversion*

Hydroconversion of 1-MN with ferrous sulfate in the presence of S, when the S/Fe ratio is 2.5 were performed at temperature from 200°C to 400°C as shown in Fig. 1. Conversions of 1-MN were very low at the reaction temperatures below 300°C. Hydroconversion of 1-MN was enhanced by the raising of reaction temperature. The conversions were 3.3%, 43% and 55% at 320°C, 350°C and 380°C, respectively. That is the conversion was increased the temperature between 320°C and 350°C. But the conversion at 400°C was only a little increase. In the case of synthetic pyrite catalyst, surface area of fresh catalyst was 13 m^2/g and surface areas of recovered catalysts after the reaction at 350°C and 400°C were 11 and 9 m^2/g, respectively. The relatively low conversion at 400°C in this paper probably suggests a

Table 2
Hydroconversion of 1-methylnaphthalene with ferric sulfate catalysts at 350°C for 1 h

Catalyst[a]	Grind[b]	Dry[c]	S-add.[d]	Structure[e]	Conv. (%)[f]	4H-select. (%)[g]	5-MT/1-MT[h]
$Fe_2(SO_4)_3 \cdot nH_2O$	Yes	No	No	$Fe_2(SO_4)_3 \cdot 8H_2O$	7.0	3.2	1.57
	Yes	Yes	No	$Fe_2(SO_4)_3 \cdot H_2O$	5.9	6.4	1.56
	Yes	No	Yes	$Fe_2(SO_4)_3 \cdot H_2O$	6.1	8.1	1.71
	Yes	Yes	Yes	$Fe_2(SO_4)_3 \cdot H_2O$	6.0	7.2	1.59

[a] Using of 2.2 Fe g-atom catalyst.
[b] Grinding of iron sulfate.
[c] Drying at 150°C for 10 h before the reaction.
[d] Sulfur addition as S/Fe atomic ratio=2.5.
[e] Main structure of catalyst before starting the reaction.
[f] Conversion of 1-methylnaphthalene.
[g] Selectivity of methyltetralins.
[h] Ratio of 5-methyltetralin/1-methyltetralin.

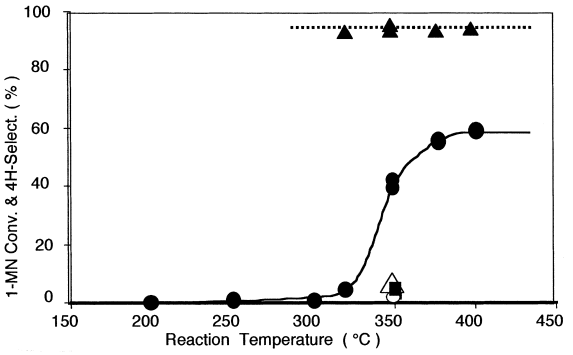


Fig. 1. Effect of reaction temperature to the conversion and tetrahydro-derivatives on 1-methylnaphthalene hydroconversion with iron sulfates. ●: conv. (%) with ($FeSO_4$+S); ▲: 4H-select. (%) with ($FeSO_4$+S); ○: conv. (%) with ($FeSO_4$+no S); ■: conv. (%) with ($Fe_2(SO_4)_3$+S); △: 4H-select. (%) with ($Fe_2(SO_4)_3$+S).

contribution of the decrease of surface area with sintering of the iron sulfides catalyst. In all cases above 320°C, the main reaction was a hydrogenation of 1-MN.

3.4. Effect of presulfiding temperature for catalysis of ferrous sulfate

The conversions as shown in Fig. 1 are including the results of three possibilities: (1) pyrrhotite formation with reaction between ferrous sulfate and elemental S or hydrogen sulfide (H_2S) formed from S, (2) hydrogenation activity with pyrrhotite produced in early stage of reaction period, and (3) the activity with the temporary active sites formed during pyrrhotites formation from the iron sulfates. The catalyst structure by means of XRD is mentioned in the Section 3.5 in detail. It is expected that the activity of pyrrhotites formed from ferrous sulfate in the presence of S is evaluated by using presulfiding of ferrous sulfate before the 1-MN hydroconversion. Fig. 2 shows effects of the temperature during presulfiding of ferrous sulfate with S addition on the 1-MN hydroconversion. The activities of iron catalysts presulfided at 300°C and 320°C increased a very little to compare with those of original sulfate. Activity of catalyst presulfided at 400°C is decreased a little. This small decrease is probably with the attribution of decrease in surface area by the sintering of pyrrhotites.

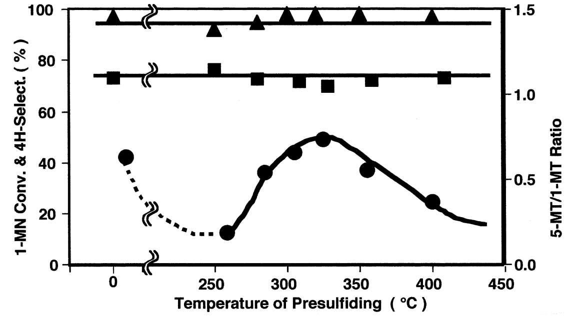


Fig. 2. Effects of presulfiding temperature on the 1-methylnaphthalene hydroconversion with ferrous sulfate catalyst in the presence of S at 350°C for 1 h (S/Fe=2.5). ●: 1-MN conversion (%); ■: 5-MT/1-MT ratio; ▲: selectivity of tetrahydro-derivatives of 1-MN (%).

3.5. Structures of iron sulfates with XRD analysis

Fig. 3 shows some XRD patterns of ferrous sulfates. Original authentic regent ferric sulfate $FeSO_4 \cdot 7H_2O$ was transformed to the mixture of much Szomolnokite ($FeSO_4 \cdot H_2O$) and a little Butlerite ($Fe(OH)SO_4 \cdot 2H_2O$) by heating at 150°C for 10 h under air. The sulfate was changed the mixture of large port of $FeSO_4 \cdot H_2O$ and a little of $Fe(OH)SO_4$ and $Fe_2S_2O_9 \cdot xH_2O$ and to light yellow solid after heating at 200°C for 10 h. The ferrous sulfate catalyst recovered after the reaction of 1-MN in decalin solvent in the

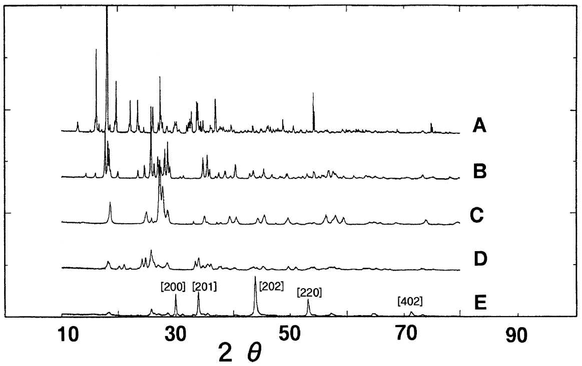


Fig. 3. XRD patterns of ferrous sulfates and the catalysts recovered after 1-methylnaphthalene hydroconversion in the absence and presence of S (S/Fe=2.5). A: original regent $FeSO_4 \cdot 7H_2O$; B: heat at 150°C for 10 h under air; C: heat at 200°C for 10 h under air; D: ferrous sulfate recovered after the reaction in the absence of S at 350°C for 1 h; E: ferrous sulfate recovered after the reaction in the presence of S at 350°C for 1 h (S/Fe=2.5).

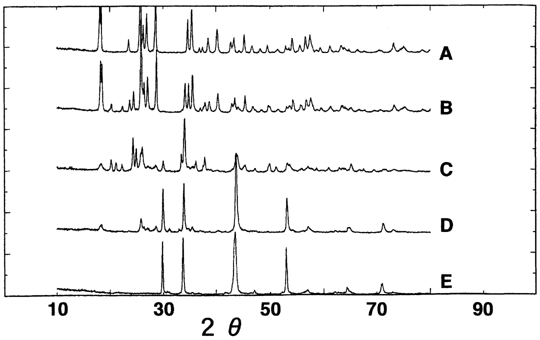


Fig. 4. Effect of reaction temperature to XRD patterns of iron catalysts after 1-methylnaphthalene hydroconversion with ferrous sulfate in the presence of elemental S (S/Fe=2.5). A: 250°C; B: 300°C; C: 320°C; D: 350°C; E: 400°C.

absence of S at 350°C was low crystallographic solid and it could not clearly recognized any confirmed structure. Ferrous sulfate, however, was transformed to pyrrhotites $Fe_{1-x}S$ structure as shown in Eq. (2). A little of ferrous sulfate remained Szomolnokite structure in the presence of S (S/Fe=2.5) at 350°C. As shown in Fig. 4, formation of $Fe_{1-x}S$ was certainly detected above 300°C by means of XRD patterns. The crystal structure of $Fe_{1-x}S$ was grown with the raising of the reaction temperature. Catalyst recovered after the reaction at 400°C was completely pyrrhotite structure.

$$FeSO_4 \cdot xH_2O + H_2S\ (\text{or S}) \rightarrow \rightarrow \rightarrow Fe_{1-x}S \quad (2)$$

On the other hand, original ferric sulfate ($Fe_2(SO_4)_3{\cdot}nH_2O$) was showed to be almost $Fe_2(SO_4)_3{\cdot}8H_2O$ by XRD and weight loss measurements. The ferric sulfate was changed to $Fe_2(SO_4)_3{\cdot}H_2O$ by heating at 150°C for 10 h. In contrast to the case of ferrous sulfate, formation of pyrrhotites from ferric sulfate was not confirmed from the reaction condition in the presence of S (S/Fe=2.5) at 350°C for 1 h, by XRD analysis as shown in Fig. 5. It suggest that sulfiding of ferric sulfate as shown in Eq. (3) is not easy.

$$Fe_2(SO_4)_3 \cdot yH_2O + H_2S\ (\text{or S}) \rightarrow \rightarrow \rightarrow Fe_{1-x}S \quad (3)$$

3.6. *Effect of sulfur additive amount to the 1-MN hydroconversion*

Structures of ferrous sulfate and ferric sulfate recovered after the reaction were affected by the amounts of S added to the reaction system at 350°C for 1 h, as shown in Figs. 6 and 7. Catalytic activities for 1-MN hydroconversion were also determined as shown in Fig. 8. Partial pressures of H_2S at S/Fe atomic ratio of 15 and 30 are estimated to be about 0.5 MPa and 1.0 MPa at room temperature, respectively. In the case of ferrous sulfate, pyrrhotites formation was confirmed at S/Fe atomic ratio over 1.1 in the reaction system from XRD analysis. The crystallinity of pyrrhotites structure increased with increase of S added. The catalytic activity of ferrous sulfate for 1-MN hydroconversion increased with the amounts of S added until a S/Fe ratio around 6. The 1-MN conver-

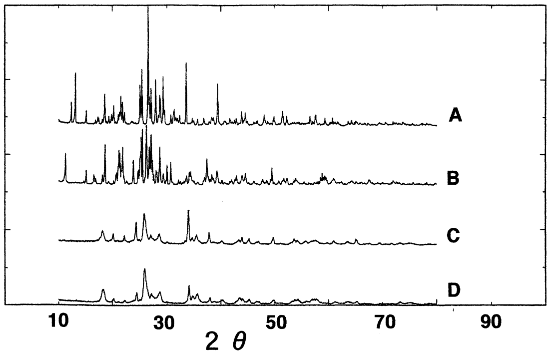


Fig. 5. XRD patterns of ferric sulfates and iron catalysts recovered after reaction with ferric sulfate in the absence and presence of S (S/Fe=2.5). A: original regent $Fe_2(SO_4)_3{\cdot}nH_2O$; B: heat at 150°C for 10 h under air; C: ferric sulfate recovered after the reaction in the absence of S at 350°C for 1 h (S/Fe=0); D: ferric sulfate recovered after the reaction in the presence of S at 350°C for 1 h (S/Fe=2.5).

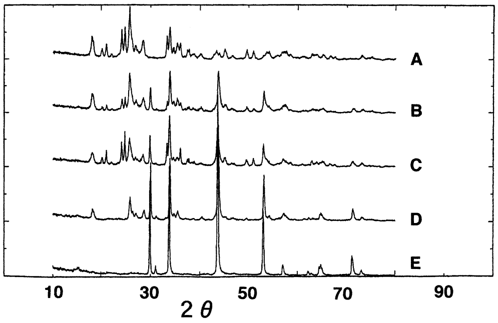


Fig. 6. Effect of additive amount of S to XRD patterns of catalysts recovered after the 1-methylnaphthalene hydroconversion with ferrous sulfate at 350°C for 1 h. Atomic ratio: A : S/Fe=0; B : S/Fe=1.11; C : S/Fe=1.26; D : S/Fe=2.50; E : S/Fe=30.

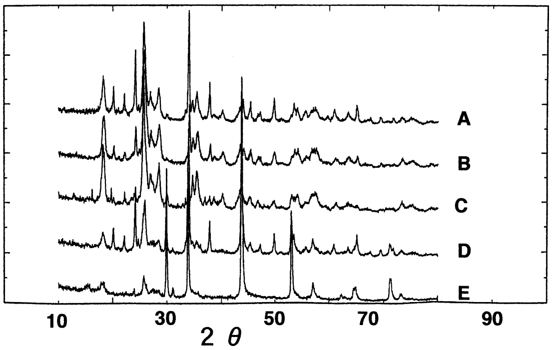


Fig. 7. Effect of additive amount of S to XRD patterns of catalysts recovered after 1-methylnaphthalene hydroconversion with ferric sulfate at 350°C for 1 h. Atomic ratio: A : S/Fe=0; B : S/Fe=2.50; C : S/Fe=6.16; D : S/Fe=15; E : S/Fe=30.

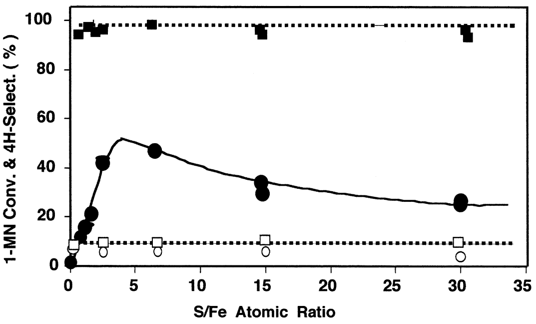
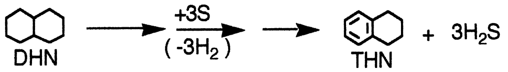


Fig. 8. Additive effects of S to the 1-methylnaphthalene hydroconversion and tetrahydro-derivatives selectivity in the presence of iron-sulfates under 10 MPa of hydrogen at 350°C for 1 h. ●: 1-MN conv. (%) ($FeSO_4$); ○: conv. (%) ($Fe_2(SO_4)_3$); ■: 4H-select. (%) ($FeSO_4$); □: 4H-select. (%) ($Fe_2(SO_4)_3$).

sion was decreased by addition of a huge excess S such as at 15 and 30 of S/Fe atomic ratio. On the other hand, pyrrhotites formation from ferric sulfate was not observed below S/Fe ratio of 2.5. Pyrrhotites formation from ferric sulfate was detected a little at S/Fe ratio of 6. Ferric sulfate, however, was transformed to almost pyrrhotites at S/Fe ratio of 30. In spite of the formation of pyrrhotites structure was confirmed, the increase of hydrogenation activity was not measured.

On the other hand, the reaction of decalin was independently performed in the presence of different amount of S added. After the reaction, elemental S in solid state was not recognized. From analysis of recovered solution, yields of tetralin and naphthalene were actually increased with increase of S added, as shown in Eqs. (4) and (5).



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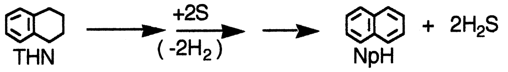

(5)

It was estimated from analysis of solution recovered that H_2S formation reaction with molecular hydrogen (H_2) was more than that from dehydrogenation of decalin. But the degree of dehydrogenation was increased with increase of S added. Further, *trans-/cis*-ratio of solvent DHN recovered was affected with amount of S added. The values of *trans-/cis*-ratio was increased with increase of S added.

3.7. *Additive effects of sulfuric acid to the reaction system*

We described before that ferrous sulfate showed catalytic activity for the hydrogenation of 1-MN in the presence of enough S and that pyrrhotites formed from ferrous sulfate were active also. But ferric sulfate showed a very low activity for aromatic-ring hydrogenation. We can consider two big differences between ferrous sulfate and ferric sulfate, that is, the oxidation state of iron and the ratio of sulfate anion (SO_4^{2-}) to iron atom in the reaction system. Oxidation states and SO_4^{2-} ion/Fe atom ratios between ferrous sulfate and ferric sulfate are Fe^{2+} and 1.0 and Fe^{3+} and 1.5, respectively. Table 3 shows that results of the additive effects of 96 wt.% sulfuric acid (H_2SO_4) to the two reaction cases in the presence of ferrous sulfate as a catalyst precursor was performed. In these two cases of sulfuric acid addition, amount of sulfate anion added had been as same amount in the case of ferric sulfate, that is, SO_4^{2-} ion/Fe atom ratio was 1.5. In first case, the additive effect of H_2SO_4 to the reaction system after pyrrhotites transformed from ferrous sulfate in the presence of S at 350°C was the effect within experimental error in conversion and the selectivity to tetrahydro-derivatives of 1-MN was decreased a little. In the case of H_2SO_4 addition from initial stage, 1-MN conversion with ferrous sulfate catalyst was dramatically

Table 3
Additive effects of sulfuric acid on 1-methylnaphthalene hydroconversion with ferrous sulfate and pyrrhotite catalyst derived from ferrous sulfate

Catalyst structure[a]	Addition of H_2SO_4[b]	Conv. of 1-MN (%)[c]	Select. of 4H (%)[d]	Ratio of 5-MT/1-MT[e]
$FeSO_4 \cdot 7H_2O$	No	43	93	1.09
$FeSO_4 \cdot 7H_2O$	Yes	4	—	—
$Fe_{1-x}S$[f]	No	40	98	1.11
$Fe_{1-x}S$[f]	Yes	39	74	0.93

[a] Catalyst structure at the start of the reaction.
[b] Addition sulfuric acid as SO_4^{2-} ion/Fe atomic ratio=1.5.
[c] Conversion of 1-MN.
[d] Selectivity of tetrahydro-derivatives of 1-MN.
[e] Molar ratio of 5-methyltetralin/1-methyltetralin.
[f] This pyrrhotite $Fe_{1-x}S$ was prepared from ferrous sulfate in the presence of S (S/Fe ratio=2.5) at 350°C for 1 h.

decreased from 43% to 4% even in the presence of same amount of S and the hydrogenated products were very decreased. It suggests that addition of 0.5M sulfate anion (SO_4^{2-}) to ferrous sulfate strongly affects to the active pyrrhotite formation process from ferrous sulfate. There is to need of more research for the elucidation of details.

4. Concluding remarks

Catalysis of iron sulfates in the 1-MN hydroconversion was investigated in the development of hydroconversion catalysts of heavy hydrocarbon materials. The catalytic activities of iron sulfates in the absence of S in the reaction system was very low in 1-MN hydroconversion. Hydrogenation activity of ferrous sulfate dramatically increased with addition of sufficient S. The hydrogenation activity of ferric sulfate, however, did not increase with addition of S. The XRD analysis of iron catalysts recovered after the reaction indicated that ferrous sulfate was transformed to pyrrhotites above 350°C in the presence of excess S in the stoichiometry. These pyrrhotites formed from ferrous sulfate showed high activity for 1-MN hydrogenation. Ferric sulfate was not easily transformed to pyrrhotites, and ferric sulfate was transformed to pyrrhotites in the presence of a huge excess of S but the 1-MN hydrogenation with this pyrrhotite did not promote. Ferrous sulfate will be one of the useful catalysts precursors for hydroconversion of heavy materials resources which include lots of sulfur and mineral matters.

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