Catalysis of α-Fe and $Fe_{1-x}S$ toward the Hydrogenolysis of *trans*-Stilbene in Hydroaromatic Hydrocarbon Solvents

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The Fe-catalyzed hydrogenolysis of *trans*-stilbene was carried out in aromatic hydrocarbon solvents at 380 °C. α-Fe and pyrrhotite catalyze bimolecular hydrogen transfer from hydroaromatic hydrocarbons to *trans*-stilbene and hydroaromatic hydrocarbon-mediated hydrogenolysis of *trans*-stilbene by molecular hydrogen at 380 °C. This catalyzed hydrogen transfer proceeds by radical mechanism. The product distribution is affected by the catalyst species. Pyrrhotite catalyzes the hydrogenation of *trans*-stilbene more effectively than α-Fe. Both the iron catalysts are inactive toward the cleavage of carbon to carbon single bond in bibenzyl.

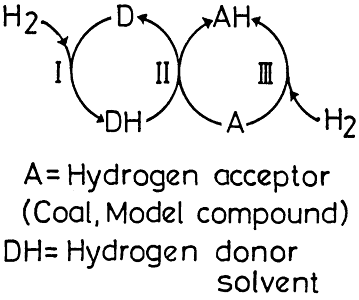
Molecular hydrogen, hydrogen donor solvents, and catalysts are the indispensable entities in coal liquefaction, and it is very important to understand the interaction among the above three and to carry out coal liquefaction under mild reaction conditions since lowering hydrogen pressure leads to reduction in the cost of coal liquids.

Hydrogen transfer reactions can be classified into three types as shown in Scheme 1: 1) direct incorporation of molecular hydrogen into coal (Step III), 2) hydrogen transfer from solvents to coal (Step II), and 3) solvent-mediated hydrogen transfer from molecular hydrogen to coal, where dehydrogenated solvents act as a hydrogen shuttler (Steps I and II). Catalysis of the Fe-compound can be expected in each step, and predominant hydrogen transfer pathways are greatly affected by the natures of solvents and catalysts, temperature, and hydrogen pressure.

The first example of catalyzed hydrogen transfer process has been reported by Guin and coworkers for the reductive deoxygenation of benzophenone by 1,2,3,4-tetrahydroquinoline, but its efficiency is low.[1)]

It is significant to clarify the interaction between solvents and catalysts in the hydrogenolysis of unsaturated bonding since aromatic units in coal are considered to decompose via partial hydrogenation of aromatic rings under coal liquefaction conditions.[2,3)]

This paper will focus on unravelling the catalysis of α-Fe and pyrrhotite ($Fe_{1-x}S$) toward the bimolecular hydrogen transfer from solvents to aromatic compounds, taking the hydrogenolysis of *trans*-stilbene in hydroaromatic hydrocarbon solvents as an example. This reaction is appropriate in modeling coal liquefaction because nearly the same propensity is observed for the hydrogen donating abilities of the solvents,[2,4)] and *trans*-stilbene can be irreversibly hydrogenolyzed under relatively mild conditions (380 °C) where almost no self-decomposition of solvents occur.



Scheme 1. Hydrogen transfer processes under coal liquefaction conditions.

Experimental

Materials. *trans*-Stilbene, bibenzyl, 1-methylnaphthalene, tetralin, and 9,10-dihydrophenanthrene were commercially purchased and purified by the conventional methods. α-Fe was prepared by reducing Fe_2O_3 in hydrogen streams at 450 °C for 20 h. Its BET surface area was 14.2 $m^2\,g^{-1}$ (Shimadzu 2200). $Fe_{1-x}S$ was prepared by reacting α-Fe with a small excess of elemental sulfur in tetralin under nitrogen at 380 °C for 30 min. Its BET surface area was 10.4 $m^2\,g^{-1}$. The above catalysts were identified by X-ray diffraction analysis (Rigaku Denki RU-200A). After preparation, they were immediately immersed in 1-methylnaphthalene or in tetralin in a dry box under nitrogen and kept until use.

Batch Experiments. A reaction solution consisting of *trans*-stilbene and a hydrocarbon solvent with or without an iron catalyst was put into a 90 ml SUS 316, magnetically stirred autoclave, pressurized by hydrogen or nitrogen. It was heated up to 380 °C within 17 min and was kept at the temperature for 30 min. After the reaction, the autoclave was cooled by an electric fan to room temperature.

Product Analysis. 6-Benzyl-1,2,3,4-tetrahydronaphthalene (BTHN) and 6-(1,2-diphenylethyl)-1,2,3,4-tetrahydronaphthalene (DETN) were isolated by combining column chromatography and vacuum distillation, and were identified by MS (JEOL JMS-DX300) and ^1H NMR (Varian EM 360A (60 MHz)) and ^{13}C NMR (JEOL JMN-GX-400 (400 MHz)).

BTHN. *m/z*: 222 (62, M^+), 131 (100), 91 (36). ^1H NMR (CCl_4) δ=1.69 (4H, m), 2.62 (4H, m), 3.77 (2H, s), 6.80 (3H, bs), 7.09 (5H, bs). ^{13}C NMR ($CDCl_3$) δ=23.24, 23.30, 29.01, 29.39, 41.59, 125.89, 126.06, 128.36, 128.85, 129.17, 129.48, 134.74, 137.06, 138.10, 141.44.

DETN. *m/z*: 312 (2.3, M^+), 221 (100), 91 (17). ^1H NMR (CCl_4) δ=1.39—2.12 (4H, m), 2.32—3.04 (4H, m), 3.21 (2H, d, *J*=7.6 Hz), 4.05 (1H, dd, *J*=7.6 Hz), 6.56—7.48 (13H, m). ^{13}C NMR ($CDCl_3$) δ=23.22, 23.24, 28.96, 29.44, 42.18, 52.75, 127.91, 128.06, 128.12, 128.30, 128.34, 128.49, 128.64, 128.92, 129.12, 134.82, 136.85, 140.46, 141.62, 144.63.

1,1′,2,2′,3,3′,4,4′-octahydrobinaphthalenes (*m/z*: 262 (22, M^+), 131 (100), 130 (68), 91 (32)) and 1,2,3,4,5′,6′,7′,8′-octahydrobinaphthalenes (*m/z*: 262 (50, M^+), 130 (100), 104 (84)) were detected by GS-MS (JEOL JMS-DX300, equipped with a glass column (4 mm diameter, 1 m length) of 5% OV-1 on Chromosorb W). The products collected with tetrahydrofuran were analyzed quantitatively by GC (Shimadzu GC-4C, equipped with a stainless column (4 mm diameter, 4 m length) of 10% OV-17 on Chromosorb W (DMCS)).

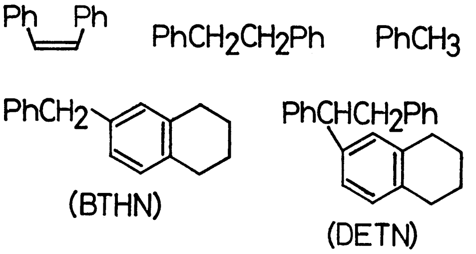


Fig. 1. Products obtained in the catalyzed hydrogenolysis of *trans*-stilbene.

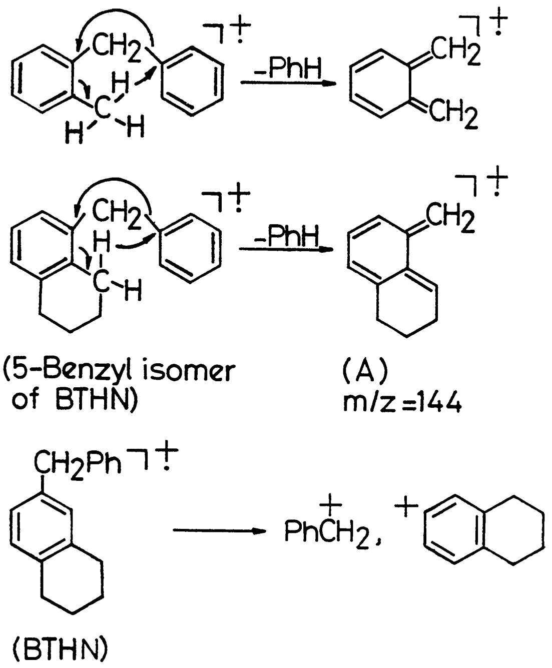


Fig. 2. Mass fragmentation patterns of 2-methyldiphenylmethane and benzyltetralins.

Results and Discussion

Physical and Chemical States of Recovered Iron Catalysts. The elemental analysis showed that the atomic ratio S/Fe of $Fe_{1-x}S$ decreased from 1.055 to 1.038 after the reaction in tetralin. This fact indicates that only 1.6% of sulphur is removed from the surface of $Fe_{1-x}S$ during the course of the reaction. According to the X-ray diffraction analysis, both α-Fe and $Fe_{1-x}S$ were recovered unchanged. Therefore, no almost change is suggested in the chemical properties of α-Fe and $Fe_{1-x}S$.

The deposition of carbonaceous materials on the catalysts was negligible since the C/Fe values of the fresh and recovered iron catalysts were 0.121—0.137, irrespective of the reaction.

The surface areas of α-Fe and $Fe_{1-x}S$ recovered from the reaction mixtures in tetralin were 12.7 and 13.0 $m^2 g^{-1}$, respectively. Therefore, rate acceleration or retardation due to surface area change could be negligible in discussing the catalysis of α-Fe and $Fe_{1-x}S$.

Structural Determination of Products. Figure 1 shows the products obtained in the Fe-catalyzed hydrogenolysis of *trans*-stilbene in tetralin.

The structure of BTHN was differentiated from that of its isomer, 5-benzyl-1,2,3,4-tetrahydronaphthalene by MS. The mass spectrum of BTHN showed only the fragment peaks assigned to tetralyl and benzyl cations, while that of the independently synthesized 5-benzyl-1,2,3,4-tetrahydronaphthalene showed another intense fragment peak at *m/z*=144 (Fig. 2). This is assigned to the fragment radical cation A formed in the migratory elimination of benzene from the radical cation of the 5-benzyl-1,2,3,4-tetrahydronaphthalene by analogy of 2-methyldiphenylmethane.[5] Under the reaction conditions, BTHN was obtained as one of the major products along with only a small amount of 5-benzyl-1,2,3,4-tetrahydronaphthalene.

The 6-substituted structure of DETN is supported since BTHN is considered to be one of the decomposition products from DETN (see below).

The structures of octahydrobinaphthalenes were also determined by MS. Both the low peak intensity of the parent ion and the base peak at *m/z*=131 strongly suggest the presence of the two benzylic and tertiary carbons in the structure of 1,1′,2,2′,3,3′,4,4′-octahydrobinaphthalene, while the base peak at *m/z*=130 suggests the migratory tetralin elimination from the parent cation radical, supporting the 2-alkylated diphenylmethane-type structure of 1,2,3,4,5′,6′,7′,8′-octahydrobinaphthalene.

In 1-methylnaphthalene and a binary solvent system of 9,10-dihydrophenanthrene and 1-methylnaphthalene, no solvent adducts were detected by GC-MS.

Tables 1—3 show the product distributions in the Fe-catalyzed hydrogenolysis of *trans*-stilbene in the three aromatic hydrocarbon solvents.

Catalysis of the Iron Compounds. Table 1 shows the effects of iron catalysts and hydrogen pressure on the hydrogenation of *trans*-stilbene in 1-methylnaphthalene. Comparison of Runs 1 and 3 shows that catalytic hydrogen transfer from 1-methylnaphthalene to *trans*-stilbene (Steps I and II) is negligible, and only about 2% of 1-methylnaphthalene is consumed in these cases. Direct hydrogenation of *trans*-stilbene by molecular hydrogen (Step III) is rather slow in the absence of

Table 1. Fe-Catalyzed Hydrogenolysis of *trans*-Stilbene in 1-Methylnaphthalene[a)]

Run	Gas phase (MPa)	Cat.	*t*-ST conv. mol%	Products (Selectivity/mol%) *c*-ST	Bibenzyl	Toluene
1	N_2 (1.0)	None	6.9	43	44	Tr.
2	H_2 (1.0)	None	10	38	50	—
3	N_2 (1.0)	α-Fe	7.4	53	36	3.6
4	H_2 (1.0)	α-Fe	26	13	62	3.8
5	H_2 (6.0)	α-Fe	44	6.6	68	3.0
6	N_2 (1.0)	$Fe_{1-x}S$	7.9	48	37	3.8
7	H_2 (1.0)	$Fe_{1-x}S$	21	18	71	3.3
8	H_2 (6.0)	$Fe_{1-x}S$	40	7.7	78	2.9

a) *trans*-Stilbene 3 g (16.7 mmol), 1-methylnaphthalene 15 g (106 mmol), reaction temperature 380 °C, reaction time 30 min. *c*- and *t*-ST=*cis*- and *trans*-stilbenes. Tr.=trace.

Table 2. Fe-Catalyzed Hydrogenolysis of *trans*-Stilbene in Tetralin[a)]

Run	Gas phase (MPa)	Cat.	*t*-ST conv. mol%	Products (Selectivity/mol%) *c*-ST	Bibenzyl	Toluene	BTHN	DETN	Naphthalene Yield/mol%
9	N_2 (1.0)	None	24	18	39	—	—	—	0.8
10	H_2 (1.0)	None	27	15	41	—	—	—	1.3
11	N_2 (1.0)	α-Fe	41	8.3	51	5.6	4.1	5.6	2.2
12	H_2 (1.0)	α-Fe	64	4.2	59	6.1	3.9	5.5	2.7
13	H_2 (6.0)	α-Fe	95	—	71	9.5	7.8	6.4	3.7
14	N_2 (1.0)	$Fe_{1-x}S$	51	6.7	69	—	—	—	2.9
15	H_2 (1.0)	$Fe_{1-x}S$	61	4.6	70	2.1	—	—	3.4
16	H_2 (6.0)	$Fe_{1-x}S$	91	—	81	1.6	—	—	3.5

a) *trans*-Stilbene 3 g (16.7 mmol), tetralin 15 ml (110 mmol), Fe catalysts 3.75 mmol of Fe, reaction temperature 380 °C, reaction time 30 min. *c*- and *t*-ST=*cis*- and *trans*-stilbenes, BTHN=6-benzyl-1,2,3,4-tetrahydronaphthalene, DETN=6-(1,2-diphenylethyl)-1,2,3,4-tetrahydronaphthalene.

Table 3. Fe-Catalyzed Hydrogenolysis of *trans*-Stilbene in 9,10-Dihydrophenanthrene-1-Methylnaphthalene[a)]

Run	Gas phase (MPa)	Cat.	*t*-ST conv. mol%	Products (Selectivity/mol%) *c*-ST	Bibenzyl	Toluene
17	N_2 (1.0)	None	21	21	56	—
18	H_2 (1.0)	None	25	16	62	—
19	N_2 (1.0)	α-Fe	24	18	58	—
20	H_2 (1.0)	α-Fe	34	12	68	—
21	H_2 (6.0)	α-Fe	71	3.2	85	—
22	N_2 (1.0)	$Fe_{1-x}S$	23	17	65	—
23	H_2 (1.0)	$Fe_{1-x}S$	44	8.0	84	—

a) *trans*-Stilbene 3 g (16.7 mmol), 9,10-dihydrophenanthrene 5 g (27.8 mmol), 1-methylnaphthalene 10 ml, Fe catalysts 3.75 mmol of Fe, reaction temperature 380 °C, reaction time 30 min. *c*- and *t*-ST=*cis*- and *trans*-stilbenes.

α-Fe in 1-methylnaphthalene (see Runs 2 and 4). $Fe_{1-x}S$ showed a comparable catalytic activity, but it was more effective as hydrogenation catalyst than α-Fe. The differences in the *trans*-stilbene conversions and in the bibenzyl yields between Runs 1, 4, and 5 give the baseline increments caused by the α-Fe-catalyzed hydrogenation of *trans*-stilbene, and comparison of Runs 1, 7, and 8 gives the corresponding increments for the $Fe_{1-x}S$-catalyzed reactions.

On the other hand, quite a different product distribution was obtained when using tetralin as solvent. Toluene and BTHN were obtained in comparable yields in the presence of α-Fe. No formation of ethylbenzene or benzene from bibenzyl in the presence of α-Fe at 380° C suggests that α-Fe cannot act as acid catalyst under the reaction conditions.[6)] 86% of the DETN decomposed in tetralin in the absence of catalyst under nitrogen at 380 °C to give BTHN and toluene in 87 and 84% selectivities, respectively. Therefore, these two products could be formed in the non-catalytic cleavage of the thermally labile C–C bond in DETN. The pathway of benzyl radical addition to tetralin is most unlikely because BTHN was not formed in the thermal decomposition of bibenzyl in tetralin under nitrogen at 380 °C.

Comparison of Runs 9, 11, and 14 clearly shows that intermolecular hydrogen transfer from tetralin to *trans*-stilbene (Step II) is greatly promoted by α-Fe and $Fe_{1-x}S$.

Bibenzyl yield increments at 6.0 MPa of hydrogen in the presence of α-Fe and $Fe_{1-x}S$ were 45 and 63%, respectively. The expected increment caused by catalytic incorporation of molecular hydrogen (Step III) is not more than 25% for α-Fe (compare Runs 2 and 5) and 26% for $Fe_{1-x}S$ (compare Runs 2 and 8). Thus, in the system of H_2-tetralin-Fe catalyst, *trans*-stilbene could be hydrogenated predominantly on the catalytic cycle (Steps I and II).

At 6.0 MPa of hydrogen in the presence of α-Fe, bitetralyls such as 1,1′,2,2′,3,3′,4,4′- and 1,2,3,4,5′,6′,7′,8′-octahydrobinaphthalenes were obtained only in 0.1% yield (Run 13). This fact suggests that coupling is the minor pathway for tetralyl radicals formed in the monohydrogen transfer from tetralin to stilbenes. No 1,2- or 1,4-dihydronaphthalene was detected by GC at this hydrogen pressure. Under the same conditions, only 3.1% of naphthalene was converted and tetralin was produced in 2.2% yield. Therefore, dihydronaphthalenes once formed, could be further dehydrogenated to inert naphthalene or hydrogenated to regenerate tetralyl radical. Tetralin could also be regenerated from 1-tetralyl radical on α-Fe.[7]

When 9,10-dihydrophenanthrene was used as hydrogen donor solvent, it was diluted with 1-methylnaphthalene due to the much higher hydrogen donating ability of 9,10-dihydrophenanthrene. In this solvent system, the iron catalysts showed similar catalytic activities as in 1-methylnaphthalene and tetralin.

In this solvent system, no solvent adduct of 1,2-diphenylethyl radical was obtained. This fact can be ascribed to the rapid capping of 1,2-diphenylethyl radical by 9,10-dihydrophenanthrene, which is a superior hydrogen donor.

Reaction Mechanism. Figure 3 shows the plot of *cis*-stilbene content against the stilbene conversion, using the data in Tables 1—3. A fairly good linear correlation suggests that the stilbene isomerization cannot be ascribed to thermochemical equilibration of *trans*- and *cis*-stilbenes. A possible intermediate could be 1,2-diphenylethyl radical, most of which is further hydrogenated to bibenzyl. There are two other minor paths for this radical: β-hydrogen release to stilbenes and addition to solvents.

In the presence of α-Fe, toluene was formed in higher yields with formation of BTHN and DETN. Since the acidity of α-Fe is negligible (see above), these findings may suggest that 1,2-diphenylethyl radical somehow stabilized on the surface of α-Fe can be trapped by tetralin solvent, and is depressed formation of radical–radical coupling products of higher molecular weights. It is interesting that the relative reactivity of 1,2-diphenylethyl radical toward addition to aromatic nuclei increases in the presence of α-Fe.

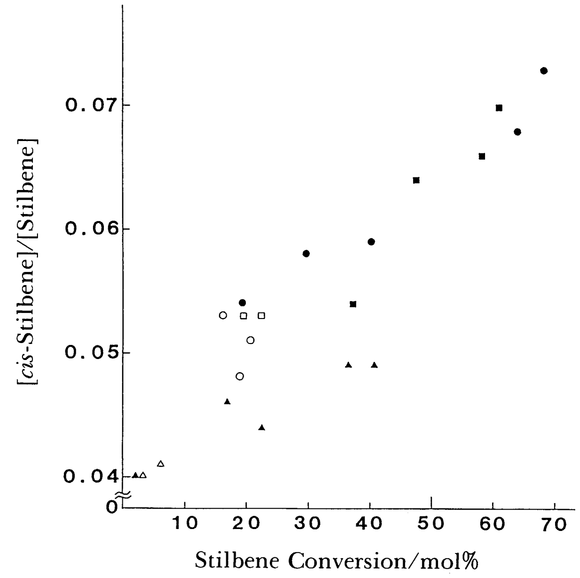
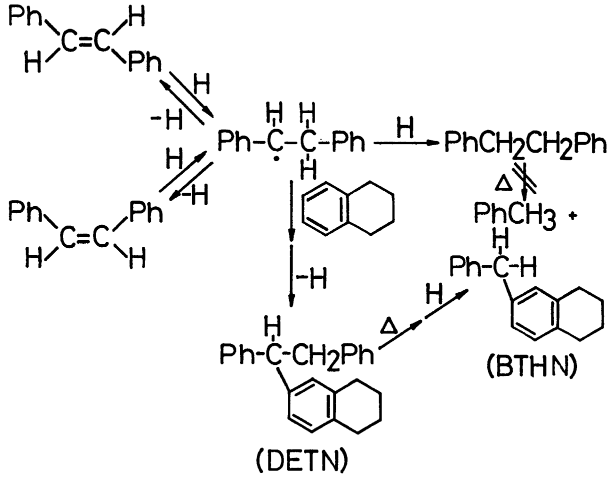


Fig. 3. Correlation of the *trans*-stilbene conversion and the *cis*-stilbene content in the hydrogenolysis of *trans*-stilbene at 380 °C. ● 9,10-Dihydrophenanthrene–1-methylnaphthalene, Fe cat. ○ 9,10-Dihydrophenanthrene–1-methylnaphthalene, no cat. ■ Tetralin, Fe cat. □ Tetralin, no cat. ▲ 1-Methylnaphthalene, Fe cat. △ 1-Methylnaphthalene, no cat.



Scheme 2. Reaction mechanism for the hydrogenolysis of *trans*-stilbene.

On the other hand, hydrogenation of 1,2-diphenylethyl radical predominates over formation of its solvent adduct on the surface of $Fe_{1-x}S$.

A plausible reaction mechanism is depicted in Scheme 2.

The chemical behavior of 1,2-diphenylethyl radical varied in the aromatic hydrocarbon solvents. The reason for this is uncertain, but adduct formation could be affected by hydrogen donating ability of solvent and stability of solvent adduct itself.

The pathway for toluene formation in 1-methylnaphthalene cannot be specified, but it is possible that a part of *trans*-stilbene adsorbed on the Fe-catalysts decomposes in the course of its hydrogenation to give benzyl radicals.

Ogawa and coworkers have shown that the catalytic activity of $Fe_{1-x}S$ highly depends on H_2S pressure in the hydrocracking of diphenylmethane without solvent at 450 °C.[8] At low pressures of H_2S, $Fe_{1-x}S$ is converted to FeS which is less active than $Fe_{1-x}S$. However, our results clearly show that both of α-Fe and $Fe_{1-x}S$ promote tetralin-mediated hydrogen transfer from gaseous hydrogen. Since dry coal liquefaction is not so feasible, the catalyzed solvent-mediated hydrogen transfer could be a key reaction in coal liquefaction.

Conclusions

1) The Fe-catalyzed hydrogenolysis of *trans*-stilbene in aromatic hydrocarbon solvents under hydrogen or nitrogen at 380 °C proceeds according to radical mechanism.

2) α-Fe and $Fe_{1-x}S$ promote bimolecular monohydrogen transfer from tetralin to *trans*-stilbene and aromatic hydrocarbon-mediated monohydrogen transfer by molecular hydrogen.

3) $Fe_{1-x}S$ is a more effective hydrogenation catalyst than α-Fe.

4) In the presence of α-Fe, addition of 1,2-diphenylethyl radical to tetralin occurs, indicating some interaction between the above radical and the surface of α-Fe.

References

1) D. G. Brook, J. A. Guin, C. W. Curtis, and T. D. Placek, *Ind. Eng. Chem., Process Des. Dev.*, **22**, 343 (1983).

2) Y. Kamiya, T. Yao, and S. Nagae, *Bull. Chem. Soc. Jpn.*, **55**, 3873 (1982).

3) S. Futamura, S. Koyanagi, and Y. Kamiya, *Fuel*, **67**, 1436 (1988).

4) Y. Kamiya, S. Futamura, T. Mizuki, M. Kajioka, and K. Koshi, *Fuel Process. Technol.*, **14**, 79 (1986).

5) S. Meyerson, H. Drews, and E. K. Field, *J. Am. Chem. Soc.*, **86**, 4964 (1964).

6) K. Tanabe and H. Hattori, *Sekiyu Gakkaishi*, **29**, 280 (1986).

7) Possibility of this reaction on sulfided iron has also been pointed out. See: T. Suzuki, O. Yamada, Y. Takahashi, and Y. Watanabe, Proceedings, Symposium on Chemistry of Coal Liquefaction and Catalysis, Sapporo, 1985, p. 190.

8) T. Ogawa, V. I. Stenberg, and P. A. Montano, *Fuel*, **63**, 1660 (1984).