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HYDROLIQUEFACTION OF COAL AND HYDROGENATION OF PHENANTHRENE WITH IRON CATALYSTS ACTIVATED BY NEW METHOD

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Iron catalysts obtained by the CO pretreatment of iron oxide and iron ore suspended in hydrocarbon solvents presented high catalytic activities for the hydroliquefaction of coal and hydrogenation of phenanthrene.

Solid catalysts are deactivated gradually by coal minerals and carbonaceous materials during direct coal hydroliquefaction.$^{1)}$ Therefore, catalyst for direct coal hydroliquefaction should satisfy at least two requirements such as high activity and moderate price because of large catalyst consumption. It is known that coal hydroliquefaction is catalyzed by iron sulfides such as pyrite or pyrrhotite,$^{2)}$ some soluble iron compounds in organic solvents,$^{3)}$ and iron oxides reduced by hydrogen.$^{4)}$ The effect of particle size on coal hydroliquefaction was studied intensively.$^{5)}$ Iron catalysts are very active when these are introduced with small amount of tin onto the coal using the ion-exchange procedure.$^{6)}$ We intended to obtain active catalysts from iron oxide and iron ore by CO pretreatments of the precursors in hydrocarbon solvents as a new preparation method.

Batch experiments of Yallourn coal hydroliquefaction(Australian brown coal) and hydrogenation of phenanthrene were performed by using two magnet-stirred autoclaves(SUS 304, 300 ml and SUS 316, 90 ml, respectively). The flow diagram for these reactions is shown in Fig. 1. The reactions are constituted with three steps such as CO pretreatment of catalyst precursors (Step I), sulfiding(Step II) and hydroliquefaction of coal or hydrogenation of phenanthrene(Step III). Iron catalysts used are iron oxide(α-Fe_2O_3), prepared by calcination of $Fe(OH)(OCOCH_3)_2$ at 500 °C in an air flow, and Iron Ore-A of iron content 40.4 wt% so called Laterite ore. Catalyst, solvent and CO or H_2 were introduced to an autoclave, and then the catalyst in the autoclave was pretreated by heating at desired temperature in electric furnace for 2 h. This process was named Reaction Step I as a pretreatment of catalysts. After the autoclave was quickly cooled down in ice-water bath, and samples of the gaseous product were collected in a sampling bag and analyzed by a gas chromatography. The autoclave which was supplemented sulfur, hydrogen and phenanthrene or coal, was heated up to and kept at the

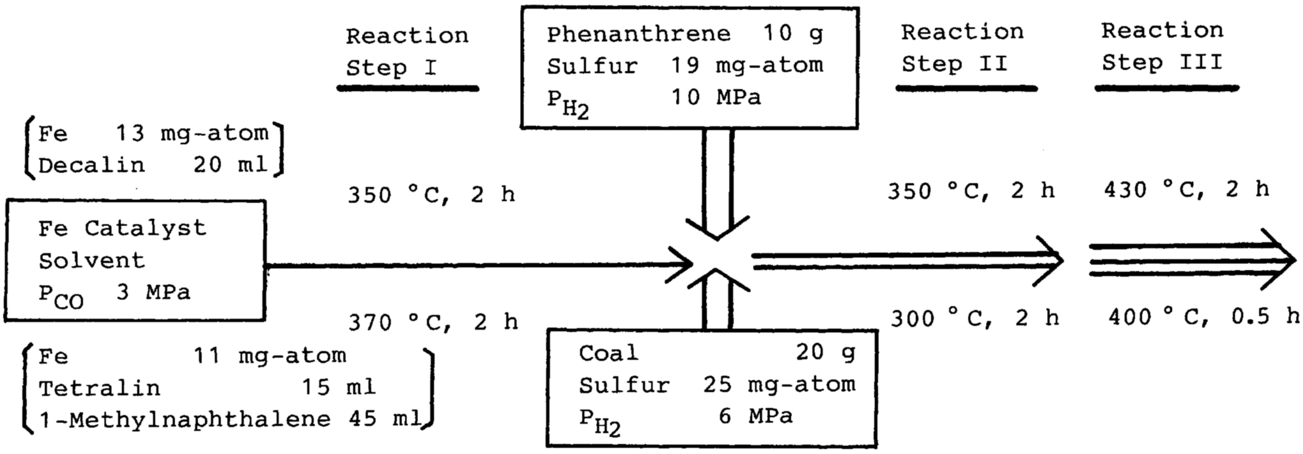

Fig. 1. Flow diagram for coal hydroliquefaction and phenanthrene hydrogenation.
Upper conditions: Phenanthrene hydrogenation.
Lower conditions: Coal hydroliquefaction.

desired temperature of Reaction Step II for a selected length of time. Step III reaction was continuously carried out at the desired temperature and time after Step II. The system was depressurized and the hydrotreated products were removed and subjected to analysis with a gas chromatography or extraction with THF in a Soxhlet apparatus.

Hydroliquefaction of coal with catalysts might be influenced by the catalytic activity for hydrogenation of aromatic rings, because aromatic structures can be cleaved via naphthenic structures. Therefore, we have chosen hydrogenation of phenanthrene as a model reaction of coal hydroliquefaction. Results of phenanthrene hydrogenation are shown in Table 1. Phenanthrene in decalin solvent was to hydrogenated in 11% conversion by hydrogen without both of catalyst and sulfur at 430 °C for 2 h. Phenanthrene conversion was increased to 16% and 22% on addition of sulfur without catalyst and iron oxide without sulfur,

Table 1. Hydrogenation of Phenanthrene with Iron Catalysts

Catalyst	none		α-Fe_2O_3					Iron Ore-A		
Run	1	2	3	4	5	6	7	8	9	10
Reaction Step I	no	no	no	no	no	yes	yes[a)]	no	no	yes
Reaction Step II	no	no	no	no	yes	yes	yes	no	yes	yes
Reaction Step III	yes[b)]	yes	yes[b)]	yes	yes	yes	yes	yes	yes	yes
Conversion(%)	11	16	22	27	45	58	44	61	66	74
Product Selectivity(mol%)										
2H-PHN[c)]	89	77	77	69	41	20	42	15	11	7
4H-PHN[d)]	16	22	32	37	31	33	34	33	37	19
Others[e)]	23	23	16	21	32	45	31	43	46	36

a)P_{H_2} 100 kg/cm^2, 350 °C, 2 h. b)Without sulfur. c)Dihydrophenanthrene. d)Tetrahydrophenanthrenes. e)Octahydrophenanthrenes + Perhydrophenanthrenes + Heavier materials than naphthalene.

respectively. The conversion of phenanthrene was increased to 27% in the presence of iron oxide(α-Fe_2O_3) catalyst and sulfur. Furthermore, the reaction with iron oxide was accelerated by pretreatment of iron oxide with 30 kg/cm^2 of carbon monoxide. Carbon dioxide is produced more than the equivalent value as shown in Eq. 1 and about 10 kg/cm^2 of pressure is decreased during the carbon monoxide

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \qquad (1)$$

pretreatment of iron oxide at 350 °C for 2 h. These results suggest that complex reactions proceeded besides reduction of iron oxide during the pretreatment becuase the reaction pressure is not decreased by simple reduction of iron oxide with carbon monoxide, as shown in Eq. 2.

$$Fe_2O_3 + CO \longrightarrow Fe_3O_4 + CO_2 \longrightarrow Fe + CO_2 \qquad (2)$$

On the other hand, the phenanthrene hydrogenation with iron oxide pretreated by hydrogen of 100 kg/cm^2 at 350 °C for 2 h, was not accelerated. But the hydrogen pressure after the hydrogen pretreatment of iron oxide decreased about 7 kg/cm^2. This phenomenon would result from the reduction of iron oxide by hydrogen as shown in Eq. 3. Phenanthrene hydrogenation with Iron Ore-A is

$$Fe_2O_3 + xH_2 \longrightarrow Fe_2O_{3-x} + xH_2O \qquad (3)$$

carried out, using the same molar equivalent of iron in cases of iron oxide catalysts. Laterite ore (Iron Ore-A) of iron content 40% as an iron catalyst precursor have shown higher activities for the hydrogenation of phenanthrene than that of iron oxide. The reaction with the iron ore catalyst pretreated with 30 kg/cm^2 of CO was accelerated such as in the cases of iron oxide(α-Fe_2O_3).

Table 2 shows the results of Yallourn coal hydroliquefaction with iron oxide and Iron Ore-A catalysts pretreated for activation. THF-soluble conversion and SRC yield or distillates were reproducible values within 1% and 3% on repeated runs, respectively. Coal conversion into tetrahydrofuran(THF) soluble materials was increased from 67% in Reaction Step III without sulfur to 77% in Reaction Steps II and III with sulfur. Coal conversions were increased to 92% and 93% with iron oxide and iron ore catalysts, respectively. Similar to phenanthrene

Table 2. Hydroliquefaction of Yallourn Coal with Iron Catalysts

Catalyst	none		α-Fe_2O_3				Iron Ore-A			
Run	11	12	13	14	15	16	17	18	19	20
Reaction Step I	no	no	no	no	yes	yes	no	no	yes	yes
Reaction Step II	no	yes	no	yes	yes	yes	no	yes	yes	yes
Reaction Step III	yes	yes	yes	yes	yes	no	yes	yes	yes	no
Coal conversion(%)$^{a)}$	67	77	92	93	94	31	93	93	96	33
SRC Yield(%)$^{b)}$	27	30	45	42	42	21	45	42	35	24
Distillates(%)$^{c)}$	40	47	47	51	52	10	48	51	61	9

a)THF-soluble conversion. b)THF-soluble residue distillated at 250 °C under 3 mmHg. c)(THF-soluble) - (SRC yield), Other symbols are same as in Table 1.

hydrogenation, coal hydroliquefactions with iron oxide and Iron Ore-A catalysts were furthur accelerated by CO pretreatment of the catalysts suspended in mixture of tetralin and 1-methylnaphthalene. These results imply that degradation activities of Ore-A catalyst on the phenanthrene hydrogenation and coal hydroliquefaction were accelerated by CO pretreatment. Coal conversions in Reaction Step II(300 °C, 1 h) were 31%(α-Fe_2O_3) and 33%(Iron Ore-A). Therefore, the flow diagram in Fig. 1 indicates that most of coal liquefaction proceeds in the Reaction Step III at 400 °C for 0.5 h.

Catalytic activities for hydrogenation of phenanthrene in the presence of solvents were improved by CO pretreatment of inexpensive iron oxide and iron ore suspended in hydrocarbon solvents as a new preparation for activation, although they were not as excellent on the hydroliquefaction of coal. These differences would be attributed to differences between hydrogenation of phenanthrene and depolymerization of coal, constituent atoms of substants such as O, N, S without C and H, and phase, aromaticity, ring size and H/C ratio of starting materials. We are investigating these problems in detail.

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