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COAL HYDROLIQUEFACTION USING IRON PENTACARBONYL AS A CATALYST PRECURSOR

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Coal hydroliquefaction using iron pentacarbonyl as a catalyst precursor was studied. The iron catalyst was found to be effective for coal liquefaction, resulting in increases in coal conversion and lighter fractions of coal derived materials.

For conversion of coal to high-quality clean liquid, catalytic hydrogenation of coal or coal derived heavy oil is of current interest. Iron catalysts such as red mud, red mud and sulfur, pyrite, ferrous sulfate, and iron ore have been widely used for coal liquefaction under hydrogen pressures.1)-3) In these cases, admixing of the insoluble iron compounds with coal-solvent slurries appears to be an important factor for the coal conversion.

To improve good contact between catalyst and coal, in this communication we have studied catalytic hydroliquefaction of coal using solvent soluble iron pentacarbonyl as a catalyst precursor, clearly indicating that iron pentacarbonyl has a high catalytic activity.

Two Japanese coals were used as samples: Taiheiyo Coal (TY: C, 77.8; H, 6.0; O(diff.), 14.9 (d.a.f.%)) and Miike Coal (MK: C, 83.9; H, 5.4; O(diff.), 7.1 (d.a.f.%)). Into a 50ml autoclave 2g of coal, 2mmol of iron pentacarbonyl, and 4ml of tetralin were charged. Hydrogen was pressurized to 50kg/cm^2 gauge, and coal hydrogenolysis was carried out at 375°C or 425°C. The reaction mixture was Soxhlet extracted with THF for 10h., then the extract was fractionated with petroleum ether and benzene to oil (petroleum ether soluble), asphaltene (AS: petroleum ether insoluble, benzene soluble), and preasphaltene (PA: benzene insoluble, THF soluble) fractions.

Iron carbonyl, soluble in common organic solvents, seems to easily permeate into cracks and micropores of coal and to decompose at a high temperature to give finely dispersed particles of metallic iron. Actually, a steep rise of the pressure was observed at around 300°C during heating up, and it appeared to be due to an evolution of carbon monoxide of iron pentacarbonyl.

The results are summarized in Table 1. In the liquefaction of Taiheiyo Coal, the presence of iron pentacarbonyl resulted in increases in the amount of the THF soluble fraction (coal conversion) from 65.7 to 85.4% at 375°C and from 90.9 to 99.7% at 425°C. In the case of Miike Coal, the THF soluble fraction increased from 96.0 to 100%. Increases in coal conversion, however, are undistinctive at 425°C in the presence of an excellent hydrogen donor solvent such as tetralin.

Benzene soluble fractions (OIL + AS) clearly increased in the presence of

Table 1 Results of Coal Liquefaction[a]

Run	Coal	Catalyst	Temp.	Conv.[b]	Product distribution			NAPH[d]	H_2abs[e]
			(°C)	(%)	OIL[c]	AS	PA (%)	(%)	(%)
1	TY	none	375	65.7	14.5	13.9	37.3	9.2	0.2
2	TY	$Fe(CO)_5$	375	85.4	26.1	12.3	47.0	4.9	1.8
3	TY	none	425	90.9	56.1	18.2	16.6	26.8	0.5
4	TY	$Fe(CO)_5$	425	99.7	56.3	25.9	17.5	15.6	3.0
5	TY	$FeSO_4$	425	92.0	57.1	19.6	15.3	27.0	0.5
6	MK	none	425	96.0	38.8	35.5	21.7	15.6	0.4
7	MK	$Fe(CO)_5$	425	∿100	45.4	39.8	14.8	7.2	1.9
8[f]	MK	Co-Mo[g]	425	92.6	46.8	33.1	12.7	15.3	1.4
9[f]	MK	$Fe(CO)_5$[h]	425	96.7	42.6	40.8	13.3	5.0	2.0

a) Coal, 2g; Fe, 2mmol; tetralin, 4ml; initial pressure of H_2, 50kg/cm^2; reaction time, 60min. unless otherwise noted. b) THF soluble fraction, based on dry, ash and catalyst free coal. c) Calculated from eq. OIL=Conv.-(AS+PA). d) Naphthalene in recovered solvent. e) Hydrogen absorbed from atmosphere, wt% to d.a.f. coal. f) Initial pressure of H_2= 100kg/cm^2. g) Mo, 12.3%; Co, 3.8% (Ketjen), 500mg. h) $Fe(CO)_5$, 0.4mmol.

iron pentacarbonyl. The fraction increased from 28.4 to 38.4% at 375°C, from 74.3 to 82.2% at 425°C for Taiheiyo Coal and from 74.3 to 85.2% for Miike Coal, respectively. Iron pentacarbonyl also promoted hydrogen absorption. The presence of iron pentacarbonyl reduced an amount of naphthalene formed from tetralin by dehydrogenation (hydrogen transfer reactions).

The catalytic effects of iron pentacarbonyl were compared with those of ferrous sulfate and a conventional hydrodesulfurization catalyst (Co-Mo on Al_2O_3) for heavy oils (see runs 4, 5, 8, and 9).[4),5)] Similar yields of coal conversion were obtained and slightly higher OIL yields were observed using ferrous sulfate and Co-Mo catalyst compared with those obtained using iron pentacarbonyl. On the other hand, the amounts of naphthalene formed in the presence of ferrous sulfate and the Co-Mo catalyst correspond to those of uncatalyzed reactions and are about as twice or three times high as those formed in the presence of iron pentacarbonyl.

The results obtained here clearly indicate that iron pentacarbonyl is active as a catalyst precursor for hydroliquefaction of coal (hydrogenation of thermally cracked fragments of coal).

References

1) D. Garg and E. N. Givens, Ind. Eng. Chem., Process Des. Dev., 21, 113 (1982).
2) C. K. Chow, Fuel, 60, 1153 (1981).
3) M. Morita, M. Ikezoe, T. Hashimoto, S. Sato, T. Imaizumi, and H. Nihei, J. Fuel Soc. Japan, 61, 42 (1982).
4) R. M. Eccles and G. R. De Vaux, Chem. Eng. Prog., 77(May), 80 (1981).
5) P. N. Ho and S. W. Weller, Fuel Proc. Technol., 4, 21 (1981).

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