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$Fe(CO)_5$/Sulfur-Catalyzed Liquefaction of Yallourn Coal in the Presence of Alcohol and Carbon Monoxide

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Iron/sulfur-catalyzed liquefaction of Yallourn coal using alcohol-carbon monoxide has been investigated. Pentacarbonyliron ($Fe(CO)_5$) /sulfur was found to be an excellent catalyst precursor. In the $Fe(CO)_5$/sulfur catalyzed liquefaction (375 °C-120 min) of Yallourn coal, high conversion (99.5%) was achieved in the presence of ethanol and CO.

Coal liquefaction has been performed mainly using highly pressurized molecular hydrogen or hydrogen donor solvents. In addition, studies on the processes by the use of alternate hydrogen sources to expensive hydrogen gas such as syngas1) or H_2O-CO,2-5) have been developed. Now, investigations on effective catalysts for these systems involving alkali metals3) and transition metals4,5) are of great importance. On the other hand, $Fe(CO)_5$/sulfur has turned out to be one of the most effective catalyst precursor in the coal liquefaction using hydrogen gas,6-9) and water-CO10) systems. In this communication, we report successful liquefaction of Yallourn coal in the presence of alcohol11) and CO by the $Fe(CO)_5$/sulfur.

Yallourn coal (C, 68.2; H, 4.5; daf%: S, 0.1; ash, 1.1 d%) (2.0 g), 1-methylnaphthalene (4.0 ml), alcohol (60 mmol), sulfur (3.0 mmol), $Fe(CO)_5$ (1.0 mmol), and a steel ball (10 mm) for mixing were placed into a 50-ml stainless-autoclave reactor. Then the system was pressurized with 7.0 MPa of CO and embedded in a heat-block with agitating for the desired reaction time. It took 5 min to reach the desired temperature. After the reaction, the gaseous sample was recovered into a gas buret and then analyzed by gas chromatography. The produced slurry was Soxhlet-extracted with tetrahydrofuran (THF) for 10 h. Conversion of coal was calculated from the amount of THF insoluble matter. The THF soluble matter was, after removal of THF, extracted with petroleum ether [boiling range = 30-60 °C] (PE). The PE soluble matter was defined as oil.12) The PE insoluble matter was separated into asphaltene (AS) and preasphalten (PA) by Soxhlet-extraction with benzene for 17 h.

Representative results are summarized in Table 1. The liquefaction of Yallourn coal using ethanol-CO as a hydrogen source at 375 °C for 60 min, in the absence of catalyst, gave

Table 1. $Fe(CO)_5$/Sulfur Catalyzed Liquefaction of Yallourn Coal in Alcohol and CO[a)]

Run	Catalyst	Alcohol	Temp °C	Time min	Conv. daf%	Oil (daf%)	AS (daf%)	PA (daf%)	H.C.gas[b)] (daf%)
1	-	EtOH	375	60	73.6	18.7	32.8	22.1	7.6
2	Fe_2O_3/S	EtOH	375	60	95.1	28.4	37.8	28.9	9.6
3	$Fe(CO)_5$/S	EtOH	375	60	97.0	25.5	48.4	23.1	8.6
4	$Fe(CO)_5$	EtOH	375	60	98.4	15.7	46.7	36.0	7.6
5	$Fe(CO)_5$/S	-	375	60	65.7	29.3	21.7	14.7	2.1
6[c)]	$Fe(CO)_5$/S	EtOH	375	60	74.8	15.8	33.9	25.1	8.3
7	$Fe(CO)_5$/S	MeOH	375	60	90.8	29.0	35.6	26.2	7.5
8	$Fe(CO)_5$/S	n-PrOH	375	60	97.1	32.5	43.3	21.3	9.9
9	$Fe(CO)_5$/S	iso-PrOH	375	60	94.9	34.5	34.9	25.5	24.2
10	$Fe(CO)_5$/S	EtOH	375	120	99.5	41.0	43.5	15.0	18.0
11	$Fe(CO)_5$/S	EtOH	375+425[d)]	60+60[d)]	94.8	59.1	24.0	11.7	35.8

a) Catalyst 1.0 mmol / Fe, Yallourn Coal 2.0 g, 1-methylnaphthalene 4.0 ml, alcohol 60 mmol, sulfur 0.096 g (3.0 mmol, in runs 1 and 4 no sulfur was added), CO 7.0 MPa (cold), b) Total yield of methane, ethylene, ethane, propylene and propane in oil fraction. The gas contains hydrocarbons derived from the alcohol, c) Ar 7.0 MPa in place of CO, d) At 375 °C for 60 min first, then at 425 °C for 60 min.

low coal conversion (73.6%) and oil yield (18.7%) (run 1). When α-Fe_2O_3/sulfur was used as a catalyst, the conversion was improved (95.1%), but AS yield (37.8%) was still low (run 2). Under the same condition, $Fe(CO)_5$/sulfur much improved the coal conversion (97.0%) and AS yield (48.4%) (run 3). In this reaction, catalytic activity was influenced by the presence of sulfur. When $Fe(CO)_5$ was used without sulfur, coal conversion was similarly high (98.4%), but oil yield was very low (15.7%) (run 4). An X-ray diffraction analysis revealed the presence of highly dispersed pyrrhotite, $Fe_{1-x}S$, in the residue of the liquefaction by $Fe(CO)_5$/sulfur. Pyrrhotite has been also formed during the reaction using molecular hydrogen in the presence of $Fe(CO)_5$/sulfur and considered to be active species.[8,13)] The reaction without ethanol or CO gave the products in low yields (runs 5 and 6), indicating both ethanol and CO are indispensable to high conversion of coal. Methanol was not an appropriate alcohol; both coal conversion (90.8%) and oil yield (29.0%) were lower than those in ethanol. n-Propanol and iso-propanol were effective as ethanol.

Figure 1 shows the time dependence of the liquefaction. The coal conversion and oil yield monotonously increased with reaction time during 120 min. Then the highest coal conversion

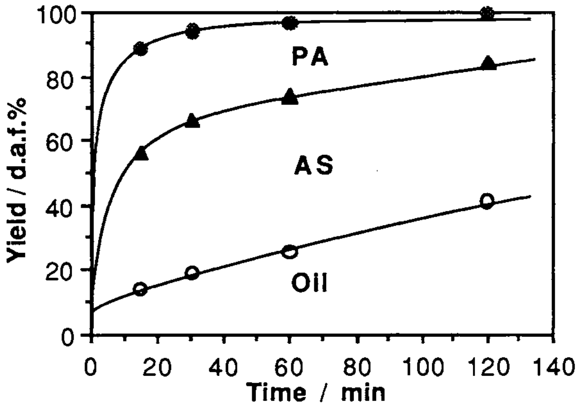

Fig.1.

Time dependence in liquefaction of Yallourn Coal. Coal 2.0 g, $Fe(CO)_5$ 1.0 mmol, sulfur 3.0 mmol, 1-methylnaphthalene 4.0 ml, EtOH 60 mmol, CO 7.0 MPa, at 375 °C.

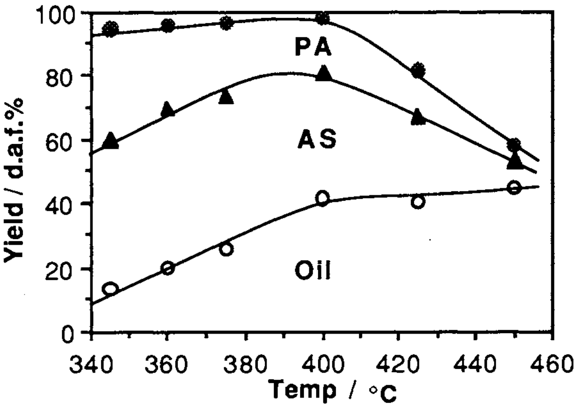

Fig. 2.

Effects of reaction temperature on liquefaction of Yallourn Coal. Coal 2.0 g, $Fe(CO)_5$ 1.0 mmol, sulfur 3.0 mmol, 1-methylnaphthalene 4.0 ml, EtOH 60 mmol, CO 7.0 MPa, for 1h.

(99.5%) and high oil yield (41.0%) were achieved in 120 min. The reaction rates in the presence of ethanol and CO was lower than those in hydrogen gas, in which 60 min was sufficient.8)

Effects of reaction temperature were examined precisely, and the results are shown in Fig. 2. The maximum coal conversion and oil yield were achieved at ca. 400 °C, and the oil yield increased as the reaction temperature was elevated. Higher reaction temperature (>400 °C) caused decrease of the coal conversion in this reaction system. The cleavage of coal structure seems to be depressed at lower reaction temperature (345 °C). At higher reaction temperature (425 °C), THF-insoluble matter would be produced by recombination of coal fragment radicals into higher molecular species.

On the other hand, the treatment of coal at lower temperature (375 °C) for 60 min prior to the reaction at higher reaction temperature (425 °C) prevented decrease in the coal conversion caused by recombination of fragment radicals mentioned above. Consequently, with $Fe(CO)_5$/sulfur as a catalyst precursor, both high coal conversion (94.8%) and high oil yield (59.1%) were achieved by two-staged heating (run 11). It is noteworthy that these values are comparable to our previous excellent results obtained in the coal liquefaction by hydrogen gas in the presence of $Fe(CO)_5$/sulfur catalyst.8)

The mass balance of the alcohol was as follows. In run 3, 60 mmol of ethanol was charged, and 25 mmol was consumed. In the produced gas, 36 mmol of CO_2 and ethylene (1.8 mmol) and ethane (4.4 mmol) were formed. As the amount of CO_2 from coal itself was estimated to be ca. 9.1 mmol,14) the amount of the hydrogen used for the liquefaction was *ca.* 2.0 wt% of the coal (d.a.f.%). This amount of hydrogen corresponds to that transformed into coal in the liquefaction by the same catalyst in H_2 gas.8)

In conclusion, we found that, in coal liquefaction, the ethanol-CO system with $Fe(CO)_5$/sulfur catalyst works very efficiently. In the reaction at 375 °C for 120 min, or in two-staged heating (375 °C-60 min then 425 °C-60 min) high conversion and high oil yield were achieved.

Studies on the following important subjects in this alcohol-CO-$Fe(CO)_5$/sulfur system are now in progress: 1) mechanism of hydrogen transfer to coal, 2) the difference in the components of each fraction obtained by the H_2O-CO system$^{10)}$ and the alcohol-CO system.

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