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$Fe(CO)_5$/Sulfur-Catalyzed Coal Liquefaction Using H_2O-CO as a Hydrogen Source

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Catalytic activity of Fe/sulfur in coal liquefaction using H_2O-CO as a hydrogen source was investigated. $Fe(CO)_5$/sulfur was found to be an excellent catalyst precursor. In the two-staged heating reaction (375 °C-60 min and 425 °C-60 min) of Yallourn coal, both high coal conversion (92.9 d.a.f.%) and high oil yield (55.8 d.a.f.%) were achieved by the $Fe(CO)_5$/sulfur catalyst.

Among various methods of coal liquefaction, several systems using H_2O-CO in place of hydrogen gas have been investigated for a long time.[1-4] Various catalysts involving alkali metals[2] and transition metals[3,4] have been investigated in this system. On the other hand, $Fe(CO)_5$/sulfur has turned out to be one of the most effective catalysts in the liquefaction using hydrogen gas.[5-8] In this communication, $Fe(CO)_5$/sulfur was found to be an excellent catalyst precursor for coal liquefaction using the H_2O-CO system.

Yallourn coal (C, 68.2; H, 4.5 daf%: S, 0.1; ash, 1.1 d%) or Wandoan coal (C, 77.1; H, 6.0 daf%: S, 0.3; ash, 9.5 d%) (2.0 g), 1-methylnaphthalene (4.0 mL), H_2O (1.1 g), sulfur (0.096 g, 3.0 mmol) and $Fe(CO)_5$ or Fe_2O_3 (0.001 g·atom-Fe) were placed into a 50-mL stainless-steel autoclave. The autoclave was charged with 7.0 MPa of CO and it was agitated for 60-120 min at the desired temperature. It took about 7 min to heat the reactor to 375 °C from ambient temperature, and in the two-staged reaction it took about 5 min to elevate the temperature to 425 °C from 375 °C. After the reaction, the reaction mixture was Soxhlet-extracted with tetrahydrofuran (THF) for 10 h. The conversion of coal was calculated from the 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.[9] The PE insoluble matter was separated into asphaltene (AS) and preasphaltene (PA) by Soxhlet-extraction with benzene for 17 h.

Representative results are summarized in Table 1. In the liquefaction of Yallourn coal at 375 °C, in the absence of catalyst, coal conversion (57.2%) and oil yield (31.8%) were very low (Run 1). When Fe_2O_3/sulfur was used as a catalyst at 375 °C, the coal conversion (75.4%) and oil yield (32.3%) were still rather low (Run 2). Under the same reaction conditions, $Fe(CO)_5$/sulfur enhanced the coal conversion drastically (95.6%) and the oil yield was improved to 37.0% (Run 3). High reaction temperature (>400 °C) caused the decrease of the coal conversion in this

reaction system (see below). However the treatment at lower reaction temperature (375 °C) for 1 h prior to the reaction at higher reaction temperature (425 °C) prevented the recombination reaction effectively. Consequently when $Fe(CO)_5$/sulfur was used as a catalyst precursor, both high coal conversion (92.9%) and high oil yield (55.8%) were achieved by two-staged heating (Run 5). It would be noteworthy that these values correspond to our previous excellent results obtained in the liquefaction of the coal by hydrogen gas in the presence of $Fe(CO)_5$/sulfur catalyst.[7]

In the liquefaction of Wandoan coal at 375 °C, both coal conversion (76.8%) and oil yield (20.6%) were very low in the absence of catalyst (Run 6). Both Fe_2O_3/sulfur and $Fe(CO)_5$/sulfur showed high coal conversion (95-97%), however, oil yield was ca. 25% (Runs 7 and 8). In the two-staged heating reaction, when $Fe(CO)_5$/sulfur catalyst was used, coal conversion was improved up to 98.5% and higher oil yield (57.0%) was achieved by conversion of AS and PA to oil (Runs 8 and 10). Also in the reaction catalyzed by Fe_2O_3/sulfur, the oil yield was improved by two-staged heating (Runs 7 and 9).

The effect of reaction temperature in the liquefaction of Yallourn coal was examined precisely and the results are shown in Fig. 1. The maximum coal conversion was achieved at 360-375 °C. It was considered that the cleavage of coal structure was depressed at lower reaction temperature (345 °C), and at higher reaction temperature (400 °C), THF-insoluble matter was produced by recombination of the coal radicals into the higher molecular species. At the higher reaction temperature, the oil yield increased with the decrease of the amounts of AS and PA.

In the present reaction, an amount of water was crucial. The effect of the amount of water is shown in Fig. 2. There is a maximum of the coal conversion at 23-35 wt% of water (coal 2.0 g, water 0.6-1.1 g). When 50 wt% of water was used (coal 2.0 g, water 2.0 g), the conversion was low (79.2%). The excess water decreases the coal conversion by an unclear reason, which we are now investigating. The maximum total pressure of the reactor at 375 °C was less than 15 MPa when 0.6 g of water was used.

It seems that the mechanism in the present reaction is different from that in the liquefaction with H_2 gas, because the pressure of H_2 gas formed from 0.6 g of water should be less than ca. 1.6 MPa (cold) which was not sufficient to convert the coal efficiently at 375 °C; more than 3.0 MPa of H_2 gas was required to achieve high coal conversion (>90%). The effect of sulfur was also very important. In the absence of sulfur, the coal conversion was very low. After the liquefaction by $Fe(CO)_5$/sulfur, iron was found as pyrrhotite, $Fe_{1-x}S$, which was confirmed by XRD analysis. Also in the liquefaction with H_2 gas by $Fe(CO)_5$/sulfur catalyst, pyrrhotite formed in the reaction mixture was assumed to be an active species.[7,11] The possibility that H_2S formed by following reactions works as a catalyst to transfer hydrogen to coal can not be ruled out.[10] Further study is required to conclude the mechanism of this reaction.

$$CO + S \longrightarrow COS$$

$$COS + H_2O \longrightarrow H_2S + CO_2$$

Table 1. $Fe(CO)_5$/Sulfur-catalyzed Liquefaction of Yallourn Coal and Wandoan Coal Using H_2O and CO[a)]

Run	Coal	Catalyst[b)]	Temp °C	Time min	Conv. daf%	Oil daf%	AS daf%	PA daf%	H.C.gas[c)] daf%
1	YL	-	375	60	57.2	31.8	14.7	10.6	1.5
2	YL	Fe_2O_3/S	375	60	75.4	32.3	23.9	19.2	1.4
3	YL	$Fe(CO)_5$/S	375	60	95.6	37.0	27.4	31.2	1.9
4	YL	Fe_2O_3/S	375-425	60+60	70.8	47.2	13.8	9.9	4.7
5	YL	$Fe(CO)_5$/S	375-425	60+60	92.9	55.8	24.2	12.8	6.1
6	WD	-	375	60	76.8	20.6	29.3	26.9	1.2
7	WD	Fe_2O_3/S	375	60	94.5	25.8	41.1	27.6	1.2
8	WD	$Fe(CO)_5$/S	375	60	96.9	25.4	47.9	23.6	1.3
9	WD	Fe_2O_3/S	375-425	60+60	94.5	38.0	35.7	20.8	4.8
10	WD	$Fe(CO)_5$/S	375-425	60+60	98.5	57.0	31.5	10.0	4.9

a) Catalyst 1.0 mg-atom-Fe, Coal 2.0 g, 1-methylnaphthalene 4.0 mL, H_2O 1.1 g, sulfur 0.096 g (3.0 mmol), CO 7.0 MPa (cold). YL= Yallourn coal. WD= Wandoan coal. b) In Run 1 and 6, no sulfur was added. c) Total yield of methane, ethylene, ethane, propylene and propane in oil fraction.

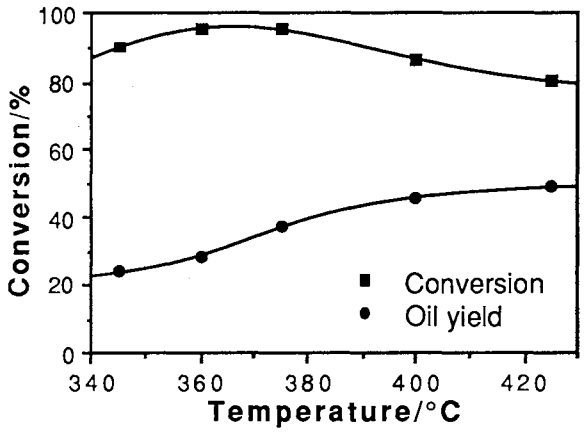

Fig. 1. The effect of reaction temperature in the liquefaction of Yallourn Coal. Coal 2.0 g, Catalyst 1.0 mg-atom-Fe, sulfur 0.096 g (3.0 mmol), 1-methyl-naphthalene 4.0 mL, H_2O 1.1 g, CO 7.0 MPa (cold), 60 min.

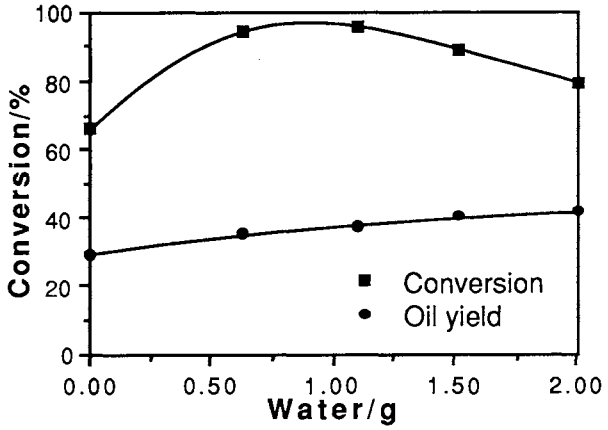

Fig. 2. The effect of amount of water in the liquefaction of Yallourn Coal. Coal 2.0 g, Catalyst 1.0 mg-atom-Fe, sulfur 0.096 g (3.0 mmol), 1-methyl-naphthalene 4.0 mL, CO 7.0 MPa (cold), 375 °C, 60 min.

The pressure of CO was also important. When CO pressure was reduced to 5.0 MPa (cold) and 3.0 MPa (cold) from the reaction conditions of Run 3, coal conversions were reduced to 89.4% and 78.2%, respectively. Raising the pressure to 9.0 MPa did not improve the coal conversion (93.8%).

In conclusion, we found that, in coal liquefaction using H_2O and CO as a hydrogen source, $Fe(CO)_5$/sulfur acted as an excellent catalyst precursor. Furthermore, under the two-staged heating reaction, both high coal conversion and high oil yield were achieved by the $Fe(CO)_5$/sulfur catalyst.

The studies on the following important subjects in this H_2O-CO-$Fe(CO)_5$/sulfur system are in progress; 1. Mechanism of hydrogen transfer to coal, involving the isotope effect using D_2O-CO. 2. The difference of the products between that obtained by pure H_2 gas and that by the CO-H_2O system which would be reflected by the mechanism of the liquefaction and the molecular structure of coal itself.

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