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$Fe(CO)_5$/Sulfur-Catalyzed Liquefaction of Yallourn Coal in Syngas-Water Systems

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Pentacarbonyliron with sulfur was found to be an excellent catalyst precursor for liquefaction of Yallourn coal using syngas-water as a hydrogen source. Both the high coal conversion and well-balanced consumption of syngas were achieved by controlling the amount of water. The two-staged reaction at 375 °C for 1 h and then at 425 °C for 1 h showed high coal conversion of 96.7% with high oil yield.

The utilization of syngas for coal liquefaction in place of hydrogen is expected to improve the process economics,(1) and several studies on this subject have been reported.(2) Some of these studies employed combined catalysts of two components, one is effective for the activation of hydrogen gas, and the other is for the water gas shift reaction.(2) The coal liquefaction with syngas and water catalyzed by iron-based catalysts of excellent activities, however, has not been well investigated.(3)

On the other hand, pentacarbonyliron ($Fe(CO)_5$) together with sulfur has been found to be an excellent catalyst precursor for coal liquefaction using hydrogen gas(4,5) or carbon monoxide-water systems.(6)

In this letter, we report the high catalytic performances of $Fe(CO)_5$/sulfur for liquefaction of Yallourn coal using syngas-water as a hydrogen source. Effects of the amount of water on coal conversion, and on the consumption of each component of syngas, hydrogen and carbon monoxide, were precisely investigated.

A typical experimental procedure is as follows: Yallourn coal (C, 68.2; H, 4.5 daf%: S, 0.1; ash, 1.1 d%, 100 mesh under, 2.0 g), 1-methylnaphthalene (4.0 mL), water (1.1 g), sulfur (0.096 g, 3.0 mmol) and $Fe(CO)_5$ or Fe_2O_3 (1.0 mmol-atom-Fe) were placed into a 50 mL micro-autoclave made of Hasteroy C with a stain-less steel ball (11 mm in diameter) to help mixing. The autoclave was charged with 3.0 MPa of carbon monoxide and 3.0 MPa of hydrogen (total 6.0 MPa cold), and then heated to 375 °C by a preheated furnace equipped with a mechanical shaker. It took about 7 min to heat the reactor to 375 °C from ambient temperature. For the two-staged reactions, it took about 5 min to heat from 375 °C to 425 °C. The reaction temperature was monitored by a sheathed CA thermocouple inserted directly into the reaction mixture. After a certain reaction period (typically 1 h), the autoclave was cooled by air blowing, and then the reaction gas was transferred into a gas bullet. The gas composition was analyzed by gas chromatography: a Porapak-Q column at 80 °C with an FID for C_1-C_4 hydrocarbons; an active carbon column with a TCD for hydrogen and carbon oxides. The apparent consumption of hydrogen or carbon monoxide was estimated by the difference of the amounts of each gas before and 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. Then the solvent (THF) of the extract was removed, and to the residue was added 200 mL of petroleum ether [boiling range; 30-60 °C (PE)], and the mixture was stirred for 1 h to precipitate asphaltene (AS) and preasphaltene (PA). The PE insoluble matter was separated into AS and PA by Soxhlet-extraction with benzene for 17 h. The coal conversion and Oil, AS and PA were calculated as follows:

$$\begin{aligned}
\text{Conversion(\%)} &= (\,1 - (\,\text{THF insolubles(g)} - \text{Ash.(g)} - \text{catalyst(g)}\,) \\
&\quad / \text{d.a.f.Coal(g)}\,) \times 100 \\
\text{Oil yield (\%)} &= \text{conversion(\%)} - \text{PE insolubles(g)} / \text{d.a.f.Coal(g)} \times 100 \\
\text{AS yield (\%)} &= \text{AS(g)} / (\,\text{AS(g)} + \text{PA(g)}\,) \\
&\quad \times \text{PE insolubles(g)} / \text{d.a.f.Coal(g)} \times 100 \\
\text{PA yield (\%)} &= \text{PA(g)} / (\,\text{AS(g)} + \text{PA(g)}\,) \\
&\quad \times \text{PE insolubles(g)} / \text{d.a.f.Coal(g)} \times 100
\end{aligned}$$

The weight of the catalyst was calculated on the basis of the following assumption; all the catalyst was left as FeS in the THF-insoluble matter. Duplicate experiments showed that coal conversions and yields of each fractions were reproducible within the range of ±0.5%.

Pentacarbonyliron /sulfur did show an excellent catalytic activity for liquefaction of Yallourn coal by syngas-water systems. Typical results are summarized in Table 1 (runs 1-6). At 375 °C with water of 0.24-0.36 g (Coal, 2.0 g; CO : H_2 = 1:1; total pressure, 6.0 MPa; 1 h), high coal conversion over 95% with oil yield of about 35% was achieved (runs 2, 3). These values were comparable to the best data obtained at the same temperature in pure carbon monoxide-water systems (run 7).[6] Although oil yields were not satisfying, almost equal coal conversions were achieved in syngas-water systems at significantly low temperature to those at 425 °C using pure hydrogen (run 10).[4,5] The amount of hydrogen transferred into coal in run 3 is calculated to be

Table 1. $Fe(CO)_5$/sulfur-catalyzed liquefaction of Yallourn coal using syngas-water as a hydrogen source[a)]

Run	Catalyst	H_2 (MPa)	CO (MPa)	H_2O (g)	Temp °C	Time min	Conv. daf%	Oil (daf%)	AS (daf%)	PA (daf%)
1	$Fe(CO)_5/S$	3.0	3.0	1.1	375	60	86.3	36.9	23.1	26.3
2	$Fe(CO)_5/S$	3.0	3.0	0.36	375	60	97.1	34.1	36.0	27.0
3	$Fe(CO)_5/S$	3.0	3.0	0.24	375	60	97.0	35.1	39.3	22.6
4	$Fe(CO)_5/S$	3.0	3.0	-	375	60	93.5	30.6	37.1	25.8
5	$Fe(CO)_5/S$	3.0	3.0	0.26	375 + 425	60 + 60	96.7	56.9	25.2	14.6
6	Fe_2O_3/S	3.0	3.0	0.36	375	60	69.8	21.7	48.1	
7	$Fe(CO)_5/S$	-	7.0	1.1	375	60	95.6	37.0	27.4	31.2
8	-	-	7.0	1.1	375	60	57.2	31.8	14.7	10.6
9	$Fe(CO)_5/S$	-	7.0	1.1	375 + 425	60 + 60	92.9	55.8	24.2	12.8
10	$Fe(CO)_5/S$	5.0	-	-	425	60	97.0	58.1	26.2	12.7

[a)] Coal; 2.0 g, catalyst; 1.0 mmol-atom-Fe, 1-methylnaphthalene; 4.0 mL, sulfur; 0.096 g (3.0 mmol); Runs 7-9 and run 10 were reported in Refs. 6 and 4, respectively.

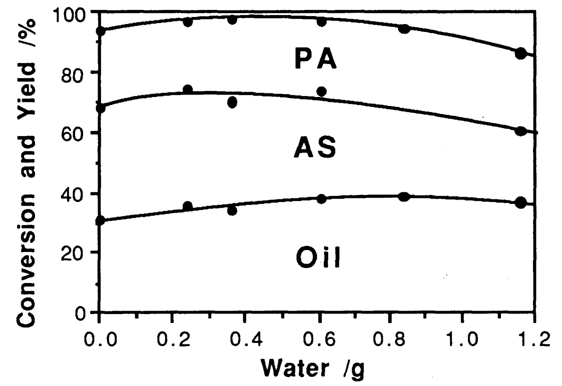

Fig. 1. Effects of amount of water on the yields. Yalourn coal; 2.0 g, 1-methylnaphthalene; 4.0 mL, CO; 3.0 MPa, H_2; 3.0 MPa, $Fe(CO)_5$; 1.0 mmol, Sulfur; 3.0 mmol, 375°C, 1 h.

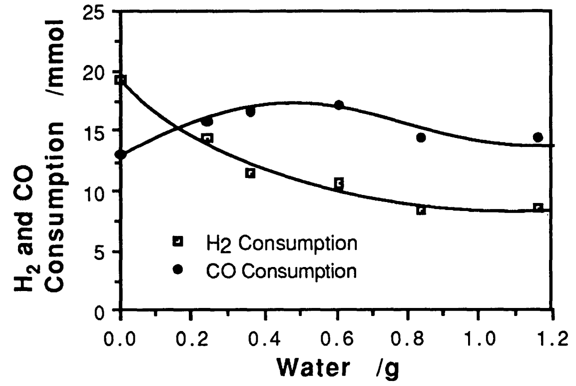

Fig. 2. Effects of amount of water on the consumptions of hydrogen and carbon monoxide. Yollourn coal; 2.0 g, 1-methylnaphthalene; 4.0 mL, CO; 3.0 MPa, H_2; 3.0 MPa, $Fe(CO)_5$; 1.0 mmol, Sulfur; 3.0 mmol, 375°C, 1 h.

ca. 3.2 wt%-coal on the basis of hydrogen consumption (14.4 mmol) and carbon dioxide formation (17.7 mmol); almost comparable to the amount of hydrogen transferred into coal observed in the liquefaction using pure hydrogen gas.(5)

As shown in run 9, the two-staged coal liquefaction with carbon monoxide-water, in which the reaction was operated at 375 °C for 1 h and 425 °C for 1 h, showed a considerably high oil yield of 55.8%. Therefore the two-staged reaction was performed using syngas-water in the present study, and the maximum oil yield of 56.9% was achieved. It should be noted that the coal conversion did not decrease, whereas in the carbon monoxide-water system the coal conversion decreased to 92.9% (run 9). The presence of molecular hydrogen would prevent the recombination of PA or AS fraction into coke during the higher temperature stage, since the reaction at 425 °C using pure hydrogen achieved both high coal conversion and high oil yield (run 10).4,5)

The catalytic activity of $Fe(CO)_5$/sulfur was much superior to that of Fe_2O_3/sulfur. The reaction by the use of Fe_2O_3/sulfur (run 6) gave considerably lower coal conversion of 69.8% and oil yield of 21.7% than those using $Fe(CO)_5$ under the same conditions (run 2).

In these reactions, the amount of water was crucial. Effects of the amount of water are shown in Fig. 1. When 0.24-0.60 g of water was used for 2.0 g of coal (at 375 °C; 1 h; CO : H_2 = 1:1; total pressure, 6.0 MPa cold), the high coal conversion of *ca.* 97% was achieved. The lack and excess of water decreased coal conversion. It should be noted that only 0.24 g of water was sufficient for coal conversion in the present study, whereas larger amount of water, 0.6-1.1 g, was required for 2.0 g of Yallourn coal in the reaction with carbon monoxide-water systems.6) Thus the operating pressure can be reduced by the use of syngas-water (12.0 MPa, with 0.3 g of water at 375 °C).

As shown in Fig. 2, the consumption of hydrogen and carbon monoxide were remarkably affected by the amount of water. When water was not added, the amount of hydrogen consumed exceeded that of carbon monoxide. The hydrogen consumption decreased with increasing amount of water. Almost equal amounts of hydrogen and carbon monoxide were consumed when ca. 0.2 g of water was used. When the output gas can be directly recycled without converting its composition, the cost of coal liquefaction would be reduced by eliminating shift convertors for recycling gases. With more than 0.2 g of water, the amount of carbon monoxide consumed exceeded that of hydrogen. However, further addition of water more than 0.60 g reduced the consumption of carbon monoxide, as observed for liquefaction by carbon monoxide-water system.6) The exact reason is still unclear.

The present results indicate that the effective coal liquefaction using syngas-water system can be operated effectively under milder conditions than those using carbon monoxide-water system, and syngas-water can be an economical alternate hydrogen source to pure hydrogen gas. The presence of the synergistic effects on the coal conversion by two hydrogen sources in the present system, molecular hydrogen and a hydride species probably produced during the water-gas shift reaction, is suggested.

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