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Coal hydroliquefaction using highly dispersed catalyst precursors

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Abstract

In order to discuss the hydrogen transfer process in coal liquefaction with a catalyst in the presence of a donor solvent, hydroliquefaction of Yallourn, Wyoming, Illinois No. 6, and Mi-ike coals and cracking of benzyl phenyl ether (BPE) were carried out in tetralin or tetralin/naphthalene mixed solvent under a hydrogen atmosphere with highly dispersed catalyst precursors such as $Fe(CO)_5$–S, $Mo(CO)_6$–S, and $Ru_3(CO)_{12}$.

In the absence of the catalyst, more than 70% of hydrogen was transferred from tetralin, as determined by the formation of naphthalene. In the presence of $Mo(CO)_6$–S and $Ru_3(CO)_{12}$, however, the amount of hydrogen transferred from tetralin decreased to 15–40% of the total hydrogen and that from gas phase increased to 60–85% of the hydrogen required to stabilize coal fragment radicals even with an excess amount of tetralin. When the reaction was carried out in the tetralin/naphthalene mixed solvent, little hydrogenation of naphthalene occurred even with the active catalyst.

This strongly supports the assertion that a decrease in the amount of naphthalene in the catalyzed liquefaction of coal in tetralin with a catalyst can be ascribed to the direct hydrogen transfer from molecular hydrogen to coal fragment radicals. In the presence of coal or benzyl phenyl ether, little or no hydrogenation of naphthalene occurred. © 1997 Elsevier Science B.V.

Keywords: Hydrogen transfer process; Coal liquefaction

1. Introduction

Conversion of coal to liquid requires a catalyst and/or a hydrogen-donor solvent. Up to now many researchers have focused on the role of hydrogen-donor solvents [1–7] and the roles of catalysts in the absence [8–15] or in the presence [16–27] of a hydrogen-donor solvent in the direct coal liquefaction. Three major roles of the catalyst were proposed in the coal liquefaction with the hydrogen-donor solvent under a hydrogen atmosphere.

The first is the hydrogenation activity of aromatic rings in the dehydrogenated solvent during the reaction [16,17,19]. Rottendorf showed that the major roles of the catalyst were to assist dissolution of the coal by rehydrogenating the donor vehicle dehydrogenated by the initial coal degradation stage and then to convert the primary tetralin-soluble products into oil by hydrogenation [17].

The second is that the catalyst promotes the direct hydrogen transfer from gas phase to coal fragment radicals [20,22–25]. Cochran indicated that in the coal liquefaction with tin-based catalyst, direct transfer of hydrogen to coal or to the fragment radicals should be involved [20]. One of the present authors pointed out that the direct hydrogen transfer reaction from molecular hydrogen to coal fragment radicals seemed to be a major reaction pathway in the coal hydroliquefaction using highly dispersed catalysts [22–24]. Charcosset

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et al. [25] reported that activated hydrogen spillover from the surface of catalysts appeared to be a more important process than the hydrogen transfer reaction from a donor solvent in the stabilization of the free radicals into coal liquid.

The last one is that the catalyst provides hydrogen from the hydrogen-donor solvent to coal, so-called transfer hydrogenation. Chow [18] proposed that Fe and Co–Mo catalyst enhanced hydrogen transfer from tetralin to coal and increased the yield of oil.

Most of the studies described above used iron species as a catalyst for the hydroliquefaction. Since the activity of iron catalyst is not high in the coal liquefaction, the roles of the catalyst and the hydrogen-donor solvent are not fully clarified.

The purpose of this study is to discuss the role of catalysts and a hydrogen-donor solvent (tetralin) in the direct coal hydroliquefaction by using highly dispersed iron, molybdenum, and ruthenium catalysts. Hydroliquefaction of various coals (Yallourn, Wyoming, Illinois No. 6 and Mi-ike coal) were carried out in tetralin or tetralin/naphthalene mixed solvent and hydrogen transfer from gas phase and tetralin were quantitatively determined. All these catalysts provided hydrogen transfer from molecular hydrogen to coal fragment radicals even in the presence of a hydrogen-donor solvent.

2. Experimental

2.1. Materials

Yallourn coal (Australia, YL, C: 68.2, H: 4.5, S: 0.1, N: 0.6 daf%; ash: 1.1 d%), Wyoming coal (USA, WY, C: 74.3, H: 5.7, S: 0.4, N: 1.1 daf%; ash: 4.8 d%), Illinois No. 6 coal (USA, IL, C: 77.3, H: 5.4, S: 3.8, N: 1.4 daf%; ash: 11.2 d%) and Mi-ike coal (Japan, MK, C: 83.9, H: 5.4, S: 1.9, N: 1.4 daf%; ash: 8.2 d%) were used in this study. All coal samples were dried, ground to pass 100 mesh sieve, and stored under an argon atmosphere.

Commercial iron pentacarbonyl ($Fe(CO)_5$; Aldrich), molybdenum hexacarbonyl ($Mo(CO)_6$; Mitsuwa Pure Chemicals) and triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$; Mitsuwa Pure Chemicals) were employed as a precursor for a highly dispersed catalyst. Benzyl phenyl ether (BPE), tetralin (TL), and naphthalene (Naph) were purchased from commercial sources and were used without further purification.

2.2. Procedures

Hydroliquefaction of coal and cracking of BPE were carried out in a batch 50 ml autoclave made of Hastelloy C. A desired amount of coal (2.0 g) or BPE (19.5 mmol) and tetralin (4.0 g) or tetralin/naphthalene (4.5 g) mixture (ratio: 8/1 in weight) were charged into the autoclave with a desired amount of catalyst (0.03–0.40 mmol). In catalyzed runs with $Fe(CO)_5$ and $Mo(CO)_6$, some molecular sulfur was added. The reactor was pressurized with hydrogen to 5.0 or 8.0 MPa at room temperature. The autoclave was heated to the desired temperature (648 or 693 K) with a preheated stainless-steel heat block equipped with a shaker. Nominal reaction time was determined from the time when the temperature of the reaction mixture had reached the desired temperature. After a given reaction time (0–60 min), the autoclave was rapidly cooled to room temperature by air blowing with an electric fan, gaseous products were collected into a gas buret, and the volume of the gas was measured.

2.3. Analyses

The gaseous products were analyzed by gas-chromatography (Shimadzu GC-8AT equipped with an activated carbon column: 3.0 mm i.d.×3 m (TCD, CO and CO_2) and Hitachi 163 equipped with a Porapack Q column: 3.0 mm i.d.×3 m (FID, C_1–C_4 hydrocarbons)). The amount of hydrogen transferred from gas phase was determined from the difference between the amounts of hydrogen charged and recovered. The amount of hydrogen charged into the autoclave was measured in a blank experiment. The amount of hydrogen recovered was determined with the gas volume collected into the gas buret and corrected for the composition of the gas.

The products in coal liquefaction were recovered from the autoclave and Soxhlet extracted with tetrahydrofuran (THF). The extract was condensed to 6 g and it was poured into 200 ml of *n*-hexane to precipitate asphaltene and preasphaltene. The precipitate was separated into asphaltene and preasphaltene by Soxhlet extraction with benzene. Coal conversion, the amount of preasphaltene (PA), asphaltene (AS), and oil fraction (Oil) were calculated as follows:

$$\text{Coal conversion (daf\%)} = \left(1 - \frac{\text{residue of THF extraction (ash and catalyst free)}}{\text{coal (daf)}}\right) \times 100,$$

$$\text{PA (daf\%)} = \frac{\text{extract with THF} - \text{residue of benzene extraction}}{\text{coal (daf)}} \times 100,$$

$$\text{AS (daf\%)} = \frac{\text{extract with benzene} - \text{residue of } n\text{-hexane extraction}}{\text{coal (daf)}} \times 100,$$

$$\text{Oil (daf\%)} = \text{Coal conversion} - (\text{PA} + \text{AS}).$$

The products derived from BPE and the solvent were identified by a gas chromatograph–mass spectrometer (GC–MS, Shimadzu QP-2000A equipped with a CBP1 (0.25 mm i.d.×25 m) capillary column) and they were quantified with FID–GC (Shimadzu GC-14AF equipped with a SE-30 column, 3.0 mm i.d.×3 m) by using an internal standard substance (cumene, ethylbenzene, pyrene, or 1-methylnaphthalene).

3. Results and discussion

3.1. Hydroliquefaction of coal in tetralin

Table 1 shows the results of hydroliquefaction of brown coal (YL and WY coal) in tetralin using Fe, Mo, and Ru catalysts. Hydroliquefaction of YL coal was carried out at 693 K in tetralin under a nitrogen or a hydrogen atmosphere at an initial pressure of 5.0 MPa (runs 1–5). In order to evaluate the role of hydrogen donor solvent, coal liquefaction was carried out under a nitrogen atmosphere without a catalyst (run 1). Very high coal conversion and oil yield were obtained even in the absence of hydrogen (conversion: 91.5%, oil yield: 50.6%). Under an initial hydrogen pressure of 5.0 MPa (run 2), coal conversion increased from 91.5% to 94.7%, and oil yield increased from 50.6% to 60.4%. Coal conversion further increased with an addition of the Fe catalyst (run 3). In catalyzed runs with the Mo and Ru catalyst, slightly high coal conversion and oil yield were obtained, even though much smaller amounts of catalyst were employed.

Runs 6–11 show the results of hydroliquefaction of WY coal in tetralin at 693 K. Coal conversion was very high, and oil yield was 42.4% even under nitrogen (run 6). In the reaction at an initial hydrogen pressure of 5.0 MPa without a catalyst (run 7), coal conversion and oil yield increased from 80.6% to 90.8% and from 42.4% to 52.6%, respectively. In the presence of Fe, Mo, and Ru catalyst (runs 8–10), coal conversion did not increase, but oil yield slightly increased to 54.2% (Fe catalyst), 56.6% (Mo catalyst), and 57.2% (Ru catalyst). Increasing Ru catalyst level to 0.08 mmol (run 11), coal conversion slightly increased to 91.7%, and oil yield markedly increased to 68.8%.

The columns indicated as DL, 1-MI, etc. and H_2 transferred in Table 1 show the composition of recovered solvent and the amounts of hydrogen transferred from gas phase and tetralin. A part of tetralin was hydrogenated to decalin, isomerized to 1-methylindan, and dehydrogenated to naphthalene. The amount of hydrogen transferred from tetralin was calculated by the amounts of naphthalene and decalin formed, assuming that all four hydrogen atoms in tetralin were utilized to stabilize coal fragment radicals. The amount of hydrogen transferred from gas phase was determined by the differences in the amount of hydrogen balances before and after the liquefaction.

In the liquefaction of YL coal without a catalyst under a nitrogen atmosphere (run 1), a large amount of naphthalene was produced, and the amount of hydrogen transferred from tetralin was calculated to be 25.8 mmol. In run 2, the amount of hydrogen transferred from gas phase increased to 8.8 mmol and that from tetralin slightly decreased from 25.8

Table 1
Hydroliquefaction of Yallourn and Wyoming coal[a]

Run	Catalyst	Metal (mmol)	Products from coal (daf%)				Products from solvent (mol%)				H_2 transferred[b] (mmol)		
			Conversion	Oil	AS	PA	DL	1-MI	Naph	TL	Gas	TL	Total
Yallourn coal													
1	None[c]	—	91.5	50.6	18.1	22.9	0.8	1.0	42.0	56.2	0.0	25.8	25.8
2	None	—	94.7	60.4	25.5	8.8	0.8	1.1	37.4	60.6	8.8	23.5	32.3
3	$Fe(CO)_5$–S[d]	0.375	97.0	63.5	24.5	9.0	1.0	1.3	27.1	70.6	15.1	16.5	31.6
4	$Mo(CO)_6$–S[e]	0.045	99.0	63.1	26.3	9.5	1.2	1.6	27.7	69.5	21.6	16.7	38.3
5	$Ru_3(CO)_{12}$	0.042	98.5	69.5	23.9	5.1	0.6	1.3	14.6	83.6	26.5	9.8	36.3
Wyoming coal													
6	None[c]	—	80.6	42.4	27.4	10.8	1.1	1.2	39.1	58.6	0.0	24.2	24.2
7	None	—	90.8	52.6	28.1	10.1	1.0	1.5	26.5	71.0	7.6	16.2	23.8
8	$Fe(CO)_5$–S[d]	0.400	90.0	54.2	27.8	8.0	0.8	1.3	9.0	88.9	21.0	4.4	25.4
9	$Mo(CO)_6$–S[e]	0.040	90.0	56.6	26.7	6.6	1.3	1.6	10.8	86.3	23.0	5.7	28.7
10	$Ru_3(CO)_{12}$	0.042	90.0	57.2	28.8	4.0	0.6	1.1	9.6	88.7	21.0	6.7	27.7
11	$Ru_3(CO)_{12}$	0.080	91.7	68.8	18.1	4.8	1.0	1.0	8.3	89.8	22.8	5.7	28.5

DL: decalin, 1-MI: 1-methylindane, Naph: naphthalene, TL: tetralin.
[a] Coal: 2.0 g, TL: 4.0 g, 693 K, 60 min, $P(H_2)=5.0$ MPa.
[b] Amount of hydrogen transferred from gas phase and tetralin.
[c] $P(N_2)=5.0$ MPa.
[d] Sulfur: 0.8 mmol.
[e] Sulfur: 0.1 mmol.

to 23.5 mmol, as compared to the reaction in nitrogen. With the addition of Fe, Mo, and Ru catalysts (runs 3–5), the amounts of naphthalene formed from tetralin decreased. Consequently, the amount of hydrogen transferred from tetralin markedly decreased and that from gas phase increased even in the presence of tetralin. The total amounts of hydrogen transferred to coal from tetralin plus gas phase increased in the presence of Fe, Mo, and Ru catalyst.

In the hydroliquefaction of WY coal in tetralin, similar findings were observed, as shown in runs 6–11.

Table 2 shows the results of the hydroliquefaction of low rank bituminous (IL) and bituminous (MK) coals at 698 K in tetralin, in order to understand general trends in hydrogen transfer process with catalyzed runs. In the run under a nitrogen atmosphere (run 12), high coal conversion was observed, but oil yield was low, and asphaltene was predominant. Under a hydrogen atmosphere without a catalyst (run 13), coal conversion and oil yield slightly increased as compared to the run in nitrogen. In the presence of the catalyst, oil yield markedly increased and asphaltene yield decreased.

Runs 17–21 show the results of the hydroliquefaction of MK coal in tetralin. Even under a nitrogen atmosphere without a catalyst, coal conversion was very high (run 17). Coal conversion increased from 95.4% to 97.6% and oil yield increased from 38.4% to 45.8% under an initial hydrogen pressure of 5.0 MPa (run 18). In the presence of a catalyst, oil yield further increased. As shown in the previous literature [12], the catalysts employed in the present work seem to affect the reaction paths from preasphaltene and asphaltene to oil fraction.

The composition of recovered solvent and the amount of hydrogen transferred after liquefaction of IL coal and MK coal in tetralin are shown in Table 2. In the liquefaction of IL coal under a nitrogen atmosphere (run 12), the amount of naphthalene formed from tetralin was 45.5 mol%. Under a hydrogen atmosphere (run 13), the amount of naphthalene formed decreased from 45.5 to 22.2 mol%, but the amount of hydrogen transferred from tetralin was larger than that from gas phase. With the addition of Fe, Mo, or Ru catalyst (runs 14–16), the amount of hydrogen transferred from tetralin (corresponding to the amount of naphthalene) decreased and that from gas phase

Table 2
Hydroliquefaction of Illinois No. 6 and Mi-ike coal[a]

Run	Catalyst	Metal (mmol)	Products from coal (daf%)				Products from solvent (mol%)				H_2 transferred[b] (mmol)		
			Conversion	Oil	AS	PA	DL	1-MI	Naph	TL	Gas	TL	Total
Illinois No. 6 coal													
12	None[c]	—	86.2	19.5	52.7	14.1	1.3	1.5	45.5	51.8	0.0	26.8	26.8
13	None	—	94.4	32.3	47.7	14.3	1.5	1.8	22.2	74.5	7.9	12.2	20.1
14	$Fe(CO)_5$–S[d]	0.375	94.9	57.8	21.9	15.3	1.3	1.9	16.1	80.7	18.0	8.6	26.6
15	$Mo(CO)_6$–S[e]	0.042	93.4	65.6	20.7	7.1	1.4	1.7	10.9	86.0	19.8	5.5	25.3
16	$Ru_3(CO)_{12}$	0.042	93.7	59.8	26.6	7.4	1.4	1.4	8.3	88.9	20.8	4.1	24.9
Mi-ike coal													
17	None[c]	—	95.4	38.4	32.6	24.5	1.1	1.2	32.3	65.4	0.0	18.8	18.8
18	None	—	97.6	45.8	37.7	14.1	1.3	1.9	22.1	74.7	3.0	14.1	17.1
19	$Fe(CO)_5$–S[d]	0.375	99.6	59.7	18.3	21.5	1.2	1.7	12.4	84.8	11.5	7.4	18.9
20	$Mo(CO)_6$–S[e]	0.050	99.9	52.6	25.4	22.0	1.0	1.1	10.7	87.3	16.9	5.8	22.7
21	$Ru_3(CO)_{12}$	0.050	98.7	50.7	36.1	11.9	1.3	1.5	9.5	87.7	11.2	6.1	17.3

DL: decalin; 1-MI: 1-methylindane; Naph: naphthalene; TL: tetralin.
[a] Coal: 2.0 g, TL: 4.0 g, 693 K, 60 min, $P(H_2)$=5.0 MPa.
[b] Amout of hydrogen transferred from gas phase and tetralin.
[c] $P(N_2)$=5.0 MPa.
[d] Sulfur: 0.8 mmol.
[e] Sulfur: 0.1 mmol.

increased as compared to the reaction without a catalyst. In the case of the hydroliquefaction of MK coal (runs 17–21), the tendency observed was similar to that in the liquefaction of IL coal.

Such results in Tables 1 and 2 show that, in the liquefaction of low rank coal (YL), larger amounts of hydrogen (32–38 mmol) were consumed, affording higher oil yields, and 43–52% of hydrogen was transferred from tetralin even with the Fe and Mo catalyst. In the liquefaction of higher rank coals (WY, IL, and MK), the amount of hydrogen consumed decreased and the contribution of the hydrogen transferred from gas phase increased with the catalyst. The molecular hydrogen was activated by the catalyst transformed from $Fe(CO)_5$–S, $Mo(CO)_6$–S, and $Ru_3(CO)_{12}$. Mo and Ru catalyst activated molecular hydrogen and increased oil yield in the liquefaction by adding a small amount of catalyst, as compared to the liquefaction with $Fe(CO)_5$–S catalyst. As shown in the previous literature [26], in the cracking of coal model compounds containing C–O bonds, the Mo and Ru catalysts contributed to the stabilization of large amounts of thermally decomposed free radicals. In the reactions of model compounds containing C–C bonds, the activity of the Fe catalyst was equal to or higher than the Mo catalyst. Consequently, it is considered that the activities of the catalyst varied with the coal rank.

According to the kinetic model of liquefaction described in the previous paper [13], in the presence of the Ru catalyst, coal fragment radicals would abstract hydrogen activated on the catalyst to give preasphaltene, asphaltene, and oil fractions. The preasphaltene further decomposes to asphaltene and oil fractions. The active catalyst would contribute to decompose preasphaltene and asphaltene into oil fraction. This was supported by the result that 23% of oil was obtained when asphaltene obtained in the liquefaction was further treated with the Ru catalyst under coal liquefaction conditions. However, according to a new kinetic model proposed for the catalyzed coal liquefaction [28], the rate constants of the consecutive reaction (preasphaltene→asphaltene→oil fraction) were small and only slightly increased even if the amount of the catalyst increased to three times as much amount. Therefore, one of the major roles of the active catalyst would be to promote the direct hydrogen transfer from gas phase to coal fragment radicals in the early stages of the liquefaction reaction.

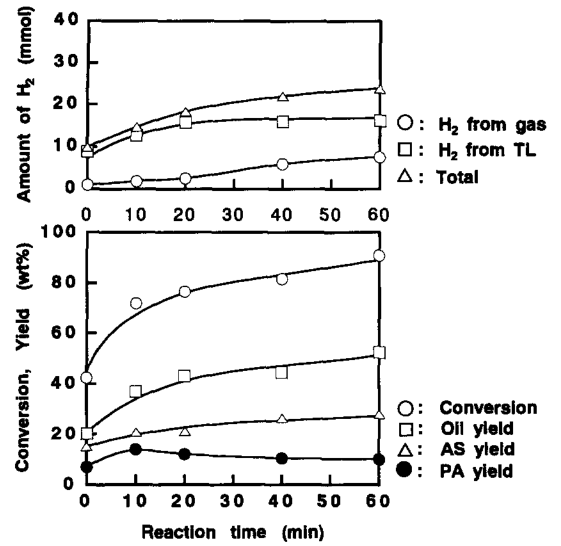

Fig. 1. Effect of reaction time on the hydroliquefaction of Wyoming coal in tetralin without catalyst: coal – 2.0 g, tetralin – 4.0 g, $P(H_2)$ – 5.0 MPa, 698 K.

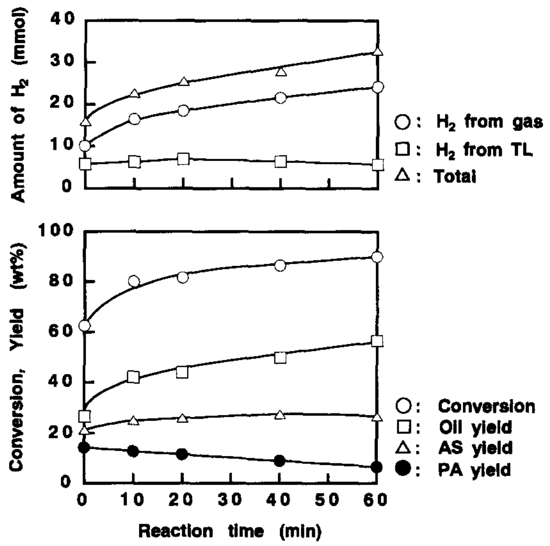

Fig. 2. Effect of reaction time on the hydroliquefaction of Wyoming coal in tetralin with Mo catalyst: coal – 2.0 g, tetralin – 4.0 g, Mo – 0.04 mmol, $P(H_2)$ – 5.0 MPa, 698 K.

3.2. *Effects of reaction time*

The effects of reaction time on the product distribution and on the amount of hydrogen transferred to coal in the liquefaction of WY coal were examined. In Fig. 1, results of the liquefaction without a catalyst are shown. Coal conversion and oil yield increased from 42.4% to 76.6% and from 20.4% to 43.2%, respectively, during the nominal reaction time from 0 to 20 min. The amount of asphaltene gradually increased from 15.2% to 28.1%, and the amount of preasphaltene showed a maximum at a reaction time of 10 min. Throughout the reaction, hydrogen was predominantly supplied from tetralin. Within the reaction time of 20 min, more than 85% of hydrogen was transferred from tetralin. The amount of hydrogen from gas phase increased from 1.0 to 8.1 mmol, with increasing the reaction time.

Figs. 2 and 3 show the effect of reaction time on the hydroliquefaction of WY coal in tetralin with $Mo(CO)_6$–S and $Ru_3(CO)_{12}$. In the hydroliquefaction with the Mo catalyst (Fig. 2), coal conversion and oil yield markedly increased from 66.6% to 81.0% and from 30.7% to 44.5%, respectively, with increasing the reaction time from 0 to 60 min. The amount of asphaltene apparently did not increase, and the amount of preasphaltene gradually decreased from 14.4% to 6.6%. The amount of hydrogen transferred from gas phase increased from 10.0 to 19.9 mmol in the nominal reaction time from 0 to 20 min, but that from tetralin did not change within experimental error.

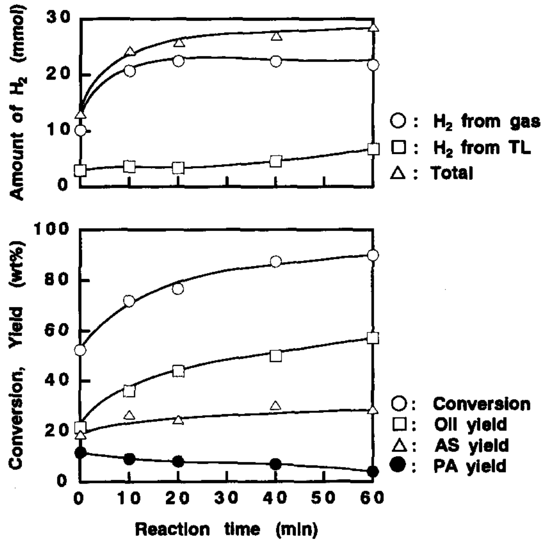

Fig. 3. Effect of reaction time on the hydroliquefaction of Wyoming coal in tetralin with Ru catalyst: coal – 2.0 g, tetralin – 4.0 g, Ru – 0.04 mmol, $P(H_2)$ – 5.0 MPa, 698 K.

Table 3
Effects of naphthalene/tetralin mixed solvent on the hydroliquefaction of Wyoming coal[a]

Run	Catalyst	Metal (mmol)	$P(H_2)$ (MPa)	Conversion (daf%)	Oil (daf%)	In feed (mmol)		In product (mmol)		D-Naph[b] (mmol)	Δ-Naph[c] (mmol)
						Naph	TL	Naph	TL		
7	None		5.0	90.8	52.6	0.0	30.3	8.0	21.5		
10	$Ru_3(CO)_{12}$	0.04	5.0	90.0	57.2	0.0	30.3	2.9	26.9	5.1	
22	$Ru_3(CO)_{12}$	0.04	5.0	96.2	61.7	3.9	30.2	6.7	26.8		
	Hypothetical					3.9	30.2	6.8			0.1
23	$Ru_3(CO)_{12}$	0.08	5.0	91.7	68.8	0.0	30.4	2.5	27.2	5.5	
24	$Ru_3(CO)_{12}$	0.08	5.0	85.1	57.5	3.9	30.3	6.4	27.3		
	Hypothetical					3.9	30.3	6.4			0.0
25	$Ru_3(CO)_{12}$	0.04	8.0	90.7	55.0	0.0	30.5	1.9	26.2	6.1	
26	$Ru_3(CO)_{12}$	0.04	8.0	87.8	47.9	3.9	30.3	4.5	26.0		
	Hypothetical					3.9	30.3	5.8			1.3
27	$Mo(CO)_6$–S[d]	0.08	5.0	95.0	66.1	0.0	30.3	3.9	25.7	4.1	
28	$Mo(CO)_6$–S[d]	0.08	5.0	92.7	60.5	3.9	30.0	8.6	24.6		
	Hypothetical					3.9	30.0	7.8			−0.8

Naph: naphthalene; TL: tetralin.
[a] Coal: 2 g, tetralin: 4.0 g, naphthalene: 0.5 g, $P(H_2)$=5.0 MPa, 693 K, 60 min.
[b] Decrease in the amount of naphthalene with a catalyst.
[c] Amount of naphthalene hydrogenated.
[d] Sulfur: 0.22 mmol.

In the hydroliquefaction with the Ru catalyst (Fig. 3), coal conversion and oil yield markedly increased in the reaction time from 0 to 60 min. The amount of asphaltene gradually increased until the reaction time of 20 min, and did not change after the reaction time of 20 min. The amount of preasphaltene slightly decreased in the nominal reaction time from 0 to 60 min. The amount of hydrogen transferred from gas phase increased from 10.0 to 22.1 mmol, but that from tetralin only slightly increased in the reaction time from 0 to 20 min.

Marked increases in coal conversion and oil yield in the initial stage seemed to indicate that oil was predominantly produced directly from coal. Oil would be gradually derived from asphaltene and preasphaltene. The amount of hydrogen transferred from tetralin (in the absence of the catalyst) and from gas phase (in the presence of the catalyst) markedly increased with increasing coal conversion and oil yield within the nominal reaction time from 0 to 60 min. Such results seem to indicate that production of oil is related to the amount of hydrogen consumption, and that in the presence of the Mo and Ru catalyst hydrogen activated on the catalyst rapidly stabilized thermally decomposed coal fragment radicals at the initial stage of coal liquefaction to give high oil yield, as described above and in the previous paper [13].

3.3. Hydroliquefaction of coal in tetralin/naphthalene mixed solvent

In the hydroliquefaction of WY coal in tetralin using finely dispersed catalysts, the amount of hydrogen transferred from gas phase markedly increased and that from tetralin decreased. Two possibilities could be proposed for the apparent decrease in the amount of hydrogen transferred from tetralin during the liquefaction.

One is the direct hydrogen transfer reaction from molecular hydrogen activated on the surface of the catalyst to thermally decomposed coal fragment radicals, resulting in the decrease in the hydrogen transfer from tetralin. The other interpretation is the hydrogenation of naphthalene dehydrogenated from tetralin through the hydrogen transfer reaction to coal fragment radicals.

As previously reported [26], the hydrogenation of naphthalene in dodecane solvent at 648 K for 60 min with $Ru_3(CO)_{12}$ catalyst afforded 26.2 mol% of tetralin by the hydrogenation of naphthalene. In order to confirm the possibility of the hydrogenation of naphthalene during coal liquefaction, the hydroliquefaction of WY coal was carried out in a tetralin/naphthalene mixed solvent under a hydrogen atmosphere using $Mo(CO)_6$–S and $Ru_3(CO)_{12}$.

The results are summarized in Table 3. In the hydroliquefaction without a catalyst (run 7), 8.0 mmol of naphthalene was produced from tetralin. In the presence of catalyst (runs 10, 23, 25 and 27), decreases in the amount of naphthalene were observed after the reaction as compared to the uncatalyzed runs. If this decrease in the amount of naphthalene is ascribed to the hydrogenation of naphthalene to tetralin, a certain amount of naphthalene in the tetralin/naphthalene mixed solvent would be hydrogenated to give tetralin. In the liquefaction with the Ru catalyst (run 10, 0.04 mmol of Ru as metal), 2.9 mmol of naphthalene was produced. As shown in run 22, 6.7 mmol of naphthalene was recovered after the reaction in the mixed solvent. Provided that the same amount of naphthalene was produced from tetralin even in tetralin/naphthalene mixed solvent (the same as run 10) and naphthalene in the mixed solvent was not hydrogenated, we could estimate 6.8 mmol of naphthalene as a hypothetical amount (3.9 mmol of naphthalene added before the reaction plus 2.9 mmol from tetralin after the reaction (run 10)). Therefore, only 0.1 mmol of naphthalene would be hydrogenated (difference in naphthalene from hypothetical value). Hydrogenation of naphthalene during the coal liquefaction would not occur, even if we increased the amount of Ru to 0.08 mmol. In the reaction with $Mo(CO)_6$–S in the mixed solvent, naphthalene would not be hydrogenated, as shown in runs 27 and 28.

In the hydroliquefaction of WY coal under an initial hydrogen pressure of 5.0 MPa with these catalysts, it is concluded that the hydrogenation of naphthalene did not occur. On the other hand, when the initial hydrogen pressure increased to 8.0 MPa (runs 25 and 26), 1.3 mmol of naphthalene was calculated to be hydrogenated with $Ru_3(CO)_{12}$ catalyst. In the reaction under higher hydrogen pressure, the hydrogenation of naphthalene occurred slightly. These results indicate that the gaseous hydrogen transfer is the main process in catalyzed coal liquefaction with a highly dispersed catalyst even in tetralin as mentioned in the previous studies [23] and that the hydrogenation of naphthalene would not occur in the hydroliquefaction under an initial hydrogen pressure of 5.0 MPa, although naphthalene was hydrogenated with $Mo(CO)_6$–S, and $Ru_3(CO)_{12}$ in dodecane solvent [26].

3.4. *Cracking of benzyl phenyl ether*

Cracking of BPE was carried out in the presence of a highly dispersed catalyst and tetralin under a hydrogen atmosphere [26]. Table 4 summarizes results of the reactions carried out under different reaction conditions. For quantitative treatment, absolute amounts of the products were listed.

H_2–R in Table 4 indicates the amounts of hydrogen required for stabilizing thermally produced organic free radicals from BPE. H_2–TL exhibits the amount of hydrogen transferred from tetralin. H_2–G shows the amount of hydrogen transferred from gas phase. Considering the experimental error, fair agreement between the amount of hydrogen required (H_2–R) and that of hydrogen transferred (H_2–G plus H_2–TL) was obtained.

H_2–R were 13.9 mmol (run 29) and 12.4 mmol (run 31) in the reactions under a hydrogen or a nitrogen atmosphere. They were predominantly supplied from tetralin (12.0 and 10.4 mmol, respectively). If we reduced the amount of tetralin to 1/4 of run 1, H_2–R remained 12.0 mmol and H_2–TL decreased to 7.5 mmol and H_2–G increased to 4.4 mmol. These results clearly show that all four hydrogen atoms in tetralin are utilized to transfer to fragment radicals when a large excess of tetralin exists in the reaction system.

In the catalyzed runs with $Mo(CO)_6$–S and $Ru(acac)_3$ (runs 34–37), the hydrogen transfer from gas phase to benzyl and phenoxy radicals proceeded more smoothly than in the uncatalyzed reactions. These catalysts increased H_2–G to 17.0 mmol (run 34) and

Table 4
Cracking of benzyl phenyl ether and the amount of hydrogen transferred to radicals[a]

Run	Catalyst	Metal (mmol)	Solv. (mmol)	PhMe (mmol)	PhOH (mmol)	DPM (mmol)	DPE (mmol)	HPPM (mmol)	BT[b] (mmol)	BN[b] (mmol)	Naph (mmol)	TL (mmol)	H_2–R[c] (mmol)	H_2–TL[d] (mmol)	H_2–G[e] (mmol)
29	None	—	28.9	11.2	13.7	1.5	0.7	4.0	0.7	0.5	5.1	19.9	13.9	12.0	0.6
30	None	—	8.8	8.7	11.8	1.8	1.0	3.9	0.3	0.6	2.9	3.1	12.0	7.5	4.4
31	None (N_2)	—	30.6	10.9	12.3	1.4	0.2	3.7	0.7	0.5	4.5	23.0	12.4	10.4	—
32	$Fe(CO)_5$–S[g]	0.400	29.1	6.0	12.8	0.3	0.9	5.3	2.5	0.6	1.8	24.6	9.6	6.3	2.6
33	$Fe(CO)_5$–S[g]	0.400	T/N[h]	7.1	12.9	0.2	0.4	4.7	3.5	1.0	4.7	25.9	10.5	4.6	6.3
34	$Mo(CO)_6$–S[i]	0.050	29.5	14.2	15.7	0.4	0.4	2.3	0.9	0.3	0.7	28.0	15.4	2.6	17.0
35	$Mo(CO)_6$–S[i]	0.050	T/N[h]	14.6	15.6	0.3	0.2	2.0	0.4	0.4	4.1	29.2	16.0	1.5	15.4
36	$Ru(acac)_3$	0.027	30.3	14.2	15.5	0.7	0.2	1.8	0.5	0.2	0.2	26.2	15.6	5.7	9.1
37	$Ru(acac)_3$	0.027	T/N[h]	13.5	14.9	0.8	0.1	2.3	0.5	0.6	5.7	26.8	15.5	4.9	11.3

DPM: diphenylmethane; DPE: 1,2-diphenylethane; HPPM: (hydroxyphenyl)phenylmethanes; Naph: naphthalene; TL: tetralin.

[a] BPE: 19.5 mmol, active carbon: 0.5 g, $P(H_2)$=5.0 MPa, 648 K, 30 min, conversion: 100%.

[b] m/z=222 (BT, benzyltetralins) and 218 (BN, benzylnaphthalenes).

[c] Calculated amount of hydrogen to stabilize radicals.

[d] Amount of hydrogen transferred from tetralin.

[e] Amount of hydrogen transferred from gas.

[f] Mol% against BPE charged.

[g] Sulfur: 0.8 mmol.

[h] Solvent: TL, 30.0 mmol; Naph, 3.9 mmol.

[i] Sulfur: 0.22 mmol.

9.1 mmol (run 37), and consequently decreases in H_2–TL were observed.

Two possibilities were proposed for such decreases in H_2–TL and increases in H_2–G in the catalyzed runs with $Mo(CO)_6$–S and $Ru(acac)_3$ in the same manner as hydroliquefaction of coal in tetralin/naphthalene mixed solvent. In order to confirm the possibility of hydrogenation of naphthalene, the cracking of BPE was carried out in tetralin/naphthalene mixed solvents, and the results are summarized in runs 33, 35 and 37 in Table 4. In the reactions in tetralin with the catalyst (runs 32, 34 and 36), 3.3–4.9 mmol of decreases in naphthalene were observed as compared to the uncatalyzed run (run 29). If these decreases are ascribed to the hydrogenation of naphthalene, a certain amount of added naphthalene would be hydrogenated to give tetralin in the reaction with mixed solvents. As seen in run 35 (with the Mo catalyst), 4.1 mmol of naphthalene was recovered. If we assume that the same amount of naphthalene was formed from tetralin (run 34) in the presence of tetralin/naphthalene mixed solvents and that no hydrogenation of added naphthalene occurred, the hypothetical amount of naphthalene after the reaction would be estimated to be 4.7 (0.7+4.0) mmol for run 35. In run 35, 4.1 mmol of naphthalene was observed, indicating that only 0.6 mmol of naphthalene was hydrogenated in the course of the reaction. The same tendency was observed in the reactions with the Ru catalyst. These results suggest that hydrogenation of naphthalene occurred slightly or not at all during the cracking of BPE. In the presence of polar substances or free radicals, the activity toward the hydrogenation of aromatic nuclei would be reduced considerably due to the stronger interaction of the catalyst with them.

The results obtained in the reactions of BPE confirmed the assumption that all the four hydrogen atoms in tetralin were utilized to stabilize coal fragment radicals in the coal liquefaction. Hydrogenation of naphthalene occurred slightly or not at all during both the coal liquefaction and the cracking of BPE. These findings indicate that the major role of the catalyst in the early stage of the liquefaction reaction would be to promote the direct hydrogen transfer reaction from gas phase to coal fragment radicals even in the presence of an abundant amount of hydrogen donor solvent. Allowing for a very small amount of the catalyst against tetralin (0.4–0.5 mmol/30 mmol), hydrogen atoms activated on the catalyst surface could be rapidly transferred to coal fragment radicals as compared to those from tetralin.

4. Conclusion

In the hydroliquefaction of Yallourn, Wyoming, Illinois No. 6, and Mi-ike coals, oil yield remarkably increased by using a highly dispersed catalyst. The amount of hydrogen transferred from tetralin was about two times as large as that from gas phase in the hydroliquefaction without a catalyst. However, the amount of hydrogen transferred from gas phase was considerably larger than that from tetralin in the hydroliquefaction of various coals with a highly dispersed catalyst.

In the hydroliquefaction of Wyoming coal, coal conversion, oil yield, and the amount of hydrogen transferred from gas phase in the reaction with a catalyst remarkably increased in the reaction time from 0 to 20 min. Little naphthalene formed from tetralin during the reaction was rehydrogenated under 5.0 MPa of hydrogen. This tendency was also confirmed in the reaction of benzyl phenyl ether using the Mo and Ru catalyst.

These results seem to indicate that the principal role of catalyst in the hydroliquefaction of coal in tetralin is to transfer molecular hydrogen to thermally decomposed coal fragments and is not to rehydrogenate naphthalene to tetralin.

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