ROLES OF MOLECULAR HYDROGEN AND A HYDROGEN DONOR SOLVENT IN THE CRACKING OF COAL MODEL COMPOUNDS WITH DISPERSED CATALYST

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Introduction

Roles of a catalyst and a hydrogen-donor solvent in the direct coal liquefaction involves still controversial arguments, because complex reactions such as thermal decomposition or hydrocracking of C-O and C-C bonds and hydrogenation of polycyclic aromatic compounds are involved in coal liquefaction reaction. Therefore, it is of great importance to evaluate quantitative hydrogen transfer process by using coal model compounds with a hydrogen-donor solvent.

Cronauer *et al.* showed that in the cracking of benzyl phenyl ether the hydrogen required to stabilize free radicals comes from a donor solvent or intramolecular rearrangement and not from gaseous hydrogen in the absence of a catalyst.[1] Korobkov *et al.*[2] and Schlosberg *et al.*[3,4] showed that the thermolysis of benzyl phenyl ether and dibenzyl ether were accomplished by intramolecular rearragements. Yokokawa *et al.* reported that tetralin retarded the catalyzed hydrocracking of coal model compounds containing C-C and C-O bonds.[5] However, few studies dealt with quantitative discussion in the hydrogen transfer process from a hydrogen-donor solvent or molecular hydrogen to free radicals derived from a model compound except a series of studies by Nicole and co-workers.[6,7]

On the other hand, it is well known that the amount of naphthalene produced from tetralin decreases after the liquefaction of coal in tetralin with catalyst as compared to the liquefaction in the absence of catalyst.[8-10] To account for this, two mechanisms are proposed. One is that the catalyst hydrogenates naphthalene produced from tetralin,[8] and the other is that the catalyst promotes the direct hydrogen transfer from molecular hydrogen to free radicals.[10,11]

The purpose of this work is to elucidate the role of catalyst and tetralin by means of the quantitative treatment of the hydrogen transfer reaction stabilizing thermally decomposed free radicals. Cracking of benzyl phenyl ether (BPE), dibenzyl ether (DBE), 1,2-diphenylethane, and 1,3-diphenylpropane was studied in tetralin in the presence of highly dispersed catalyst.

Experimental

Cracking of coal model compounds was carried out in a batch 50 mL autoclave made of Hastelloy C. Prescribed amounts of a model compound (3.6 - 3.9 g, 19.5 mmol), a catalyst (0.01 - 0.08 g, 0.025 - 0.4 mmol), tetralin (4.0 g, 30.0 mmol) or tetralin/naphthalene (4.0 g / 0.5 g, 30.0 mmol / 4.0 mmol), and an activated carbon (0.5 g) as a dispersing agent for the catalyst were put into the autoclave. Activated carbon was added in uncatalyzed runs, in order to elucidate catalytic effect of activated carbon. In catalyzed runs with $Fe(CO)_5$ and $Mo(CO)_6$, a molecular sulfur was added.

The reactor was pressurized with a hydrogen to 5.0 MPa at a room temperature. The autoclave was heated to the desired temperature (648 or 698 K) with a preheated stainless-steel heat block equipped with a shaker. After a given reaction time (20 - 240 min.), the autoclave was cooled to room temperature by air blowing. The gas was collected into a gas buret. The liquid products were recovered from the autoclave by filtering off the activated carbon with a sintered glass filter, followed by repeated washing with tetrahydrofuran.

The amount of hydrogen transferred from gas phase was determined with the difference between the amount of hydrogen charged and recovered.

Results and Discussion

Cracking of Benzyl Phenyl Ether. Table I summarizes results of the reactions carried out under different reaction conditions by using several catalysts. Conversion of BPE was 100 % in all cases at 648 K for the reaction time of 30 min.

As shown in Scheme I, the identified products from cracking of BPE were benzene (PhH), toluene (PhMe), phenol (PhOH), diphenylmethane (DPM), 1,2-diphenylethane (DPE), isomeric (hydroxyphenyl)phenylmethanes (HPPM), benzyltetralins[7] (BT, m/z=222 in GC-MS), and benzylnaphthalenes[7] (BN, m/z=218 in GC-MS). The major products were PhMe and PhOH, and the other products such as DPM and DPE were minor. BPE was thermally decomposed at a relatively low temperature and seemed to produce quantitatively benzyl radical and phenoxy radical, and these radicals abstract hydrogen from tetralin or benzyl radical may combine with tetralyl radical. The material balances between charged BPE and recovered products in these reactions were good to very good and in the range of 87 mol% to 98 mol%. The products formed from tetralin were naphthalene, decalin and 1-methylindan.

H_2-R in Table I indicates the amounts of hydrogen required for stabilizing thermally produced organic free radicals from BPE. They were calculated from the amounts of cracked products assuming the following over all stoichiometric reactions (not showing exact chemical path).

$$\text{Ph-CH}_2\text{O-Ph} \rightarrow \text{Ph-CH}_2 + \text{Ph-O}\cdot \quad (1)$$

$$\text{Ph-CH}_2\cdot + 3\text{H} \rightarrow \text{Ph-H} + \text{CH}_4 \quad (2)$$

$$\text{Ph-CH}_2\cdot + \text{H} \rightarrow \text{Ph-CH}_3 \quad (3)$$

$$\text{Ph-O}\cdot + \text{H} \rightarrow \text{Ph-OH} \quad (4)$$

$$\text{Ph-CH}_2\text{-(C}_6\text{H}_4\text{)-OH} + 2\text{H} \rightarrow \text{Ph-CH}_2\text{-Ph} + \text{H}_2\text{O} \quad (5)$$

The rest of the products such as DPE and HPPM can be produced by the recombination of radicals or rearrangements of BPE, and no hydrogen were required.[7] H_2-TL in Table I exhibits the amount of hydrogen transferred from tetralin. It was calculated from the amount of naphthalene and decalin formed by the dehydrogenation and the hydrogenation of tetralin, assuming that all four hydrogens in tetralin are utilized. 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.

In the reaction without catalyst (Run 1) the amounts of PhMe and PhOH were 11.3 mmol and 13.7 mmol respectively, these amounts were smaller than those in the reactions with $Mo(CO)_6$-S and $Ru(acac)_3$. The reaction in a smaller amount of tetralin (Run 2 BPE/TL= 2), the amounts of PhMe and PhOH further decreased and those of DPM and DPE slightly increased.

The amount of hydrogen required for stabilizing free radicals (H_2-R) were 13.9 mmol (Run 1) and 12.4 mmol (Run 3) in the reactions under a hydrogen or a nitrogen atmosphere. They were predominantly supplied from tetralin (12.0 mmol and 10.4 mmol respectively). These results clearly show that all four hydrogen atoms in tetralin are utilized to transfer to fragment radicals. With a decrease in the tetralin concentration contribution of hydrogen in gas phase increased even in the absence of catalyst (Run 2 probably catalyzed by wall).

$$R\cdot + TL \rightarrow RH + TL\cdot \quad (6)$$

$$2TL\cdot \rightarrow TL + DHN\ (\text{dihydronaphthalene}) \quad (7)$$

$$R\cdot + DHN \rightarrow RH + DHN\cdot \quad (8)$$

$$DHN\cdot + TL\cdot (\text{or } DHN\cdot) \rightarrow Naph + TL\ (\text{or } DHN) \quad (9)$$

$$R\cdot + TL\cdot \rightarrow R\text{-}TL \quad (10)$$

$$R\cdot \xrightarrow{H_2/\text{catalyst}} RH \quad (11)$$

$$TL\cdot \xrightarrow{H_2/\text{catalyst}} TL \quad (12)$$

The amount of hydrogen absorbed slightly increased with $Fe(CO)_5$-S, although ten times larger amount of Fe was used in these runs as compared to Mo and Ru. The ability of $Fe(CO)_5$-S catalyst to activate molecular hydrogen seems not to be high.

In the reactions with $Mo(CO)_6$-S (Runs 6 - 8), or $Ru(acac)_3$ (Runs 9-11) the amounts of toluene and phenol increased, and the amount of HPPM decreased correspondingly. These results indicate that the hydrogen transfer from gas phase to benzyl radical and phenoxy radical proceeded more smoothly than in the uncatalyzed reactions. Decreases in H_2-TL and increases in H_2-G in the catalyzed runs with $Mo(CO)_6$-S and $Ru(acac)_3$ suggest the possibility of direct hydrogen transfer from gaseous hydrogen to benzyl and phenoxy radicals more efficiently (equation 11).

Cracking of Dibenzyl Ether. Cracking of DBE was carried out under the same condition as the cracking of BPE except that the reaction time was shortened to 20 min. The results are summarized in Table II. The identified products from cracking of DBE were benzene, toluene, benzaldehyde (PhCHO), benzyl alcohol (BA), 1,2-diphenylethane, benzyltetralins, and benzylnaphthalenes. H_2-R was calculated according to the following over all stoichiometric equations (not showing exact chemical paths).

$$Ph\text{-}CH_2OCH_2\text{-}Ph \rightarrow Ph\text{-}CH_2\cdot + Ph\text{-}CH_2O\cdot \quad (13)$$

$$Ph\text{-}CH_2\cdot + 3H \rightarrow Ph\text{-}H + CH_4 \quad (14)$$

$$Ph\text{-}CH_2\cdot + H \rightarrow Ph\text{-}CH_3 \quad (15)$$

$$Ph\text{-}CH_2\cdot + Ph\text{-}CH_2O\cdot \rightarrow Ph\text{-}CH_3 + Ph\text{-}CHO \quad (16)$$

$$Ph\text{-}CH_2O\cdot + H \rightarrow Ph\text{-}CH_2OH \quad (17)$$

$$Ph\text{-}CH_2O\cdot + 3H \rightarrow Ph\text{-}CH_3 + H_2O \quad (18)$$

It is noteworthy in these reactions that PhMe was produced more than the amount that was evaluated from equations 15 and 16. An excess amount of PhMe could be originated from the hydrogenation of oxygen containing compound as shown in equation 18. Amount of H_2O was about 14.2 mmol, corresponding to the occurrence of reaction 18. Estimated H_2-R was smaller than H_2-G plus H_2-TL due to unidentified minor products in most catalyzed runs.

As shown in Table II, in the uncatalyzed reactions at 648 K (Runs 12 in H_2 and Run 13 in N_2) the amounts of PhMe were 23.2 and 23.1 mmol and those of PhCHO were 6.1 and 7.5 mmol respectively indicating the lowest yields of PhMe and the highest yields of PhCHO. In addition under a nitrogen atmosphere DPE increased to 3.2 mmol, suggesting that the recombination of benzyl radicals most likely proceeded. On the other hand, H_2-R (15.1 mmol) is in fair agreement with H_2-TL (14.7 mmol), indicating that most of hydrogen required to stabilize fragment radicals transferred from tetralin.

When $Fe(CO)_5$-S was employed for the cracking of DBE (Runs 14 and 15), the amounts of H_2-TL and H_2-G (15.4 mmol and 1.9 mmol in Run 14) were approximately same as those in the uncatalyzed run (14.7 mmol and 0.5 mmol in Run 12). However, H_2-TL decreased to 9.0 mmol and H_2-G increased to 9.8 mmol when smaller amount of tetralin was used (8.0 mmol, Run 15). The amount of PhCHO (2.1 mmol in Run 14) was less than that in Run 12 (6.1 mmol). These results suggest that the possibility of direct hydrogen transfer from gaseous hydrogen to benzyl and Ph-$CH_2O\cdot$ radicals to form toluene is enhanced.

In the catalyzed runs with $Mo(CO)_6$-S and $Ru(acac)_3$ (Runs 16 and 19), PhCHO and BA were scarcely detected and PhMe was increased to 27.5 mmol and 29.6 mmol suggesting considerable possibility of reaction 18. Although H_2-R was estimated to be smaller than H_2-G plus H_2-TL due to unidentified minor products, correspondingly increases in H_2-R could be expected. Furthermore,

with these catalysts, decreases in H_2-TL to 1/3 of the H_2-R (11.7 and 9.2 mmol) and increases in H_2-G to about 80 % of H_2-R (22.5 and 22.7 mmol) were observed similar to the reaction with BPE. However, in the reaction with $Mo(CO)_6$-S the amount of H_2-TL was larger than that in the cracking of BPE with the same catalyst. The contribution of tetralin for the hydrogen transfer process to stabilize the thermally decomposed free radicals increased in the cracking of DBE. Whereas, if we decreased the amount of tetralin to 8 mmol (Run 17 and 20), H_2-TL decreased to 5.5 and 4.6 mmol and H_2-G increased to 25.7 and 27.3 mmol as seen in the reaction with $Fe(CO)_5$-S, suggesting that the possibility of direct hydrogen transfer from gaseous hydrogen to radicals increased.

Cracking of benzyl phenyl ether and dibenzyl ether in tetralin-naphthalene mixed solvent. In the cracking of BPE and DBE in tetralin using finely dispersed catalyst, two possibilities were proposed for the decrease in the amount of naphthalene after the reactions. One is the direct hydrogen transfer process from molecular hydrogen activated on the catalyst to free radicals, consequently contribution of the hydrogen transfer from tetralin to free radicals decreased. The other is the hydrogenation of naphthalene formed after hydrogen transfer to radicals with catalyst. In order to confirm the possibility of hydrogenation of naphthalene, the cracking of BPE or DBE was carried out in tetralin/naphthalene mixed solvents, and the results are summarized in Runs 8, 11, 18 and 21 in Tables I and II.

In the reactions in tetralin with the catalyst (Runs 4, 6 and 9), 3.3 - 4.9 mmol of decreases in naphthalene were observed as compared to the uncatalyzed run (Run 1 in Table I). 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 Runs 8 and 11, 4.1 and 5.7 mmol of naphthalene was recovered respectively. If we assume that the same amount of naphthalene was formed from tetralin (Runs 6 and 9) in the presence of tetralin-naphthalene mixed solvents and no hydrogenation of added naphthalene did occur, hypothetical amount of naphthalene after the reaction would be estimated to be 4.7 (0.7 + 4.0) and 4.2 (0.2 + 4.0) mmol for Runs 8 and 11, respectively. In Run 8, 4.1 mmol of naphthalene was observed, indicating that only 0.6 mmol of naphthalene was hydrogenated in the course of the reaction. In Run 11, 5.7 mmol of naphthalene was detected. This is rather increase in 1.5 mmol of naphthalene, as compared to the hypothetical amount of naphthalene. These results suggest that hydrogenation of naphthalene did not or slightly occurred during the cracking of BPE. As shown in Runs 18 and 21 in Table II, hydrogenation of naphthalene during the reaction was also examined in the cracking of DBE. It was found that 0 - 1.3 mmol of naphthalene was hydrogenated in the course of cracking of DBE.

In separate experiments, hydrogenation of naphthalene or naphthalene in tetralin did proceed considerable extent with all the catalysts employed here. Thus 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.

On the other hand, 0.3 mmol to 2.1 mmol of BT were produced in the cracking of BPE and DBE even with the active catalyst such as $Mo(CO)_6$-S and $Ru(acac)_3$, and BT increased in the cracking of DBE at 698 K. This seems to provide possibility of formation of tetralyl radical which in turn combined with benzyl radical or were hydrogenated to tetralin on the catalyst surface as proposed in the previous study.[12] Cochran *et al.* have suggested that the direct hydrogen transfer is the predominant route in tin-catalyzed coal liquefaction.[10] Importance of molecular hydrogen in the catalyzed coal liquefaction with highly dispersed catalysts has been pointed out by Charcosset et al.[13] The direct hydrogen transfer from gas phase hydrogen activated on the catalyst not only to free radicals derived from BPE or DBE but also tetralyl radical.

Cracking of 1,2-diphenyl ethane and 1,3-diphenylpropane Cleavage of C-C bonds in coal is much more important reactions in the hydroliquefaction of subbituminous or bituminous coal. In order to examine catalytic effects of dispersed catalyst on the dissociation of C-C bond, 1,2-DPE and 1,3-diphenylpropane (1,3-DPP) in tetralin was carried out without or with dispersed catalysts. Results are summarized in Table III. Cracked products are benzene, toluene, and ethylbenzen, in addition to small amounts of BT and BN.

Much lower conversions were obtained in both model compounds even at higher reaction temperature of 425 °C and longer reaction period of 60 min. In the absence of catalyst, the amount of hydrogen required to stabilize thermally cracked free radical is in good agreement with the amount of hydrogen produced from tetralin calculated from the amount of naphthalene formed (see Runs 22 and 23).

With the addition of dispersed catalysts not significant differences in the amounts of cracked products were observed, indicating poor capability of metal sulfides or metal species on the hydrocracking of C-C bond. Due to the lower conversion of model compounds, the amounts of hydrogen absorbed from gas phase could not be measured accurately. However, the amount of naphthalene formed after the reaction decreased as compared to the run without catalyst, when a smaller amount of tetralin was employed. Such phenomena were pronouncedly observed, when $Mo(CO)_6$-S and $Ru(acac)_3$ catalysts were used. In these cases (Runs 27 and 30), the amount of hydrogen required to stabilize free radicals from DPE exeeded the amount of hydrogen dehydrogenated from tetralin. This indicates that hydrogen transfer from molecular hydrogen to organic radicals on the catalyst occurred. However, in the abundant hydrogen donor solvent, hydrogen transfer from tetralin to benzy radical did proceed more effectively to give toluene.

Such tendencies are seen in the cracking of DPP. Only Ru based catalyst effectively promoted hydrogen transfer from gas phase hydrogen to organic free radicals.

These results indicate that C-C bonds in the coal model structure were thermally dissociate to give free radicals and they abstract hydrogen to give stable organic compounds either from a hydrogen donor solvent or molecular hydrogen activated on the catalsyst. However, even in the

presence of an active catalsyst, hydrogen was pronouncedly supplied to such hydrocarbon radicals from a hydrogen donor solvent like tetralin.

Two reasons for this can be proposed. One is that due to a higher bond dissociation energy of C-C bonds in the model compounds, the rate of benzyl radical formation is small, and consequently abundant hydrogen donor solvent could provide hydrogen to organic free radicals. The other is that benzyl radical could be less strongly adsorbed on the active catalyst as compared to the oxygen containing free radicals derived from BPE and DBE. Therefore, hydrogen transfer from gas phase to benzyl radical only slightly occurred.

Conclusion

Quantitative hydrogen transfer process from tetralin to organic free radicals was clarified. Direct hydrogen transfer from molecular hydrogen on the dispersed catalyst was proposed for the cracking of oxygen containing coal model compounds, in the presence of hydrogen donor such as tetralin.

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Table 1 Cracking of Benzyl Phenyl Ether and the Amount of Hydrogen Transferred to Radicals[a]

Run	Catalyst	Solv. mmol	PhMe	PhOH	DPM	DPE	HM	BT[b]	BN[b]	Naph	TL	H_2-R[c]	H_2-T[d]	H_2-G[e]
			mmol											
1	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
2	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
3	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	—
4	$Fe(CO)_5$-S[f]	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
5	$Fe(CO)_5$-S[f]	8.1	8.8	12.2	0.4	1.2	4.3	0.4	0.5	2.4	4.4	9.8	4.2	6.6
6	$Mo(CO)_6$-S[g]	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
7	$Mo(CO)_6$-S[g]	8.3	12.4	14.5	0.8	0.5	2.5	0.6	0.4	0.9	6.2	14.3	3.0	15.5
8	$Mo(CO)_6$-S[g]	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
9	$Ru(acac)_3$	30.3	14.2	15.5	0.7	0.2	1.8	0.5	0.2	2.0	26.2	15.6	5.7	9.1
10	$Ru(acac)_3$	8.2	13.3	16.1	0.7	0.7	2.0	0.6	0.4	0.9	6.1	15.4	3.0	19.3
11	$Ru(acac)_3$	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

a) BPE 19.5mmol, active carbon 0.5g, $P(H_2) = 5.0$MPa, reaction time 30min, 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) Sulfur 0.8mmol. g) Sulfur 0.22mmol. h) Solvent : TL, 30.0mmol; Naph, 4.0mmol.

Abbreviations : DPM, diphenylmethane; DPE, 1,2-diphenylethane;

HM, (hydroxyphenyl)phenylmethanes; Naph, naphthalene; TL, tetralin.

Table II Cracking of Dibenzyl Ether and the Amount of Hydrogen Transferred to Radicals [a]

Run	Catalyst	Solv.	PhMe	PhCHO	BA	DPE	BT[b]	BN[b]	Naph	TL	H_2-R[c]	H_2-T[d]	H_2-G[e]
				mmol							mmol		
12	none	29.8	23.2	6.1	trace	1.2	0.6	1.0	6.4	21.1	15.1	14.7	0.5
13	none(N_2)	30.1	23.1	7.5	1.6	3.2	0.4	0.8	5.6	21.7	19.8	13.6	—
14	$Fe(CO)_5$-S [g]	29.3	24.3	2.1	—	1.0	1.6	2.4	4.4	16.3	21.9	15.4	1.9
15	$Fe(CO)_5$-S [g]	8.3	22.8	3.8	—	1.7	0.3	1.3	2.8	3.1	18.1	9.0	9.8
16	$Mo(CO)_6$-S [i]	30.0	27.5	—	trace	1.4	1.8	1.7	3.3	21.4	27.9	11.7	22.5
17	$Mo(CO)_6$-S [i]	8.1	25.7	—	—	2.0	0.9	1.1	2.0	4.0	29.8	5.5	25.7
18	$Mo(CO)_6$-S [i]	T/N [h]	25.2	trace	—	1.2	1.7	1.9	6.0	23.3	24.8	8.7	21.0
19	$Ru(acac)_3$	30.2	29.6	0.7	trace	0.8	1.2	0.7	3.4	22.8	27.9	9.2	22.7
20	$Ru(acac)_3$	8.0	29.0	trace	—	1.4	0.8	0.7	1.3	5.0	28.9	4.6	27.3
21	$Ru(acac)_3$	T/N [h]	29.6	trace	—	0.7	1.1	0.8	6.7	25.2	29.4	7.5	25.0

a) DBE 19.5mmol, active carbon 0.5g, $P(H_2)$ = 5.0 MPa, reaction time 20min,
b) m/z=222 (BT, benzyltetralins) and 218 (BN, benzylnaphthalenes).
c) Amount of hydrogen transferred to radicals.
d) Amount of hydrogen from tetralin. e) Amount of hydrogen from gas.
f) Mol percent against DBE charged. g) Sulfur 0.8mmol.
h) Solvent : TL, 30.0mmol; Naph, 4.0mmol. i) Sulfur 0.22mmol.
Abbreviations : BA, benzyl alcohol; DPE, 1,2-diphenylethane; Naph, naphthalene; TL : tetralin.

Table III Cracking of 1,2-diphenylethane and 1,3-diphenylpropane in tetralin[a]

Run	Catalyst	metal	Time	Solv	PhH	PhMe	PhEt	Naph	TL	H_2-R	H_2-TL
		mmol	min				mmol				
			Diphenylethane								
22	None		60	8.3	0.86	5.20	0.83	1.4	5.7	3.3	2.9
23	None		60	30.1	0.53	5.30	0.46	2.1	25.4	3.1	4.2
24	None		240	29.9	1.47	15.74	1.67	5.3	17.6	9.4	10.6
25	$Fe(CO)_5$-S	0.40	60	8.3	0.92	5.81	1.06	1.2	5.5	3.9	2.3
26	$Fe(CO)_5$-S	0.40	60	29.5	0.52	5.31	0.55	2.8	24.2	3.2	5.5
27	$Mo(CO)_6$-S	0.05	60	8.2	0.93	4.96	0.97	0.8	6.5	3.2	1.6
28	$Mo(CO)_6$-S	0.05	60	28.8	0.69	6.03	0.99	5.6	19.1	4.0	11.1
29	$Mo(CO)_6$-S	0.05	240	30.9	1.43	17.20	2.03	5.9	16.8	10.6	11.9
30	$Ru(acac)_3$	0.025	60	8.1	0.88	4.92	0.86	0.9	5.8	3.3	1.8
31	$Ru(acac)_3$	0.025	60	30.0	0.49	5.72	0.53	2.3	24.8	3.4	4.6
			Diphenylpropane								
32	None		60	4.1	0.13	1.36	1.14	0.54	2.1	1.3	1.1
33	$Fe(CO)_5$-S	0.06	60	4.12	0.11	1.99	2.07	0.82	2.6	2.1	1.6
34	$Mo(CO)_6$-S	0.08	60	4.11	0.22	1.99	1.95	1.05	2.3	2.1	2.1
35	$Ru(acac)_3$	0.04	60	4.11	0.18	2.01	2.12	0.42	3.27	2.16	0.9

a) Diphenylethane: 19.5 mmol, Diphenyl propane: 2.5 mmol active carbon 0.50 g, 425 °C, PH_2= 5.0 MPa,
Other abbreviations are the same as Table I.