

Analysis Of Initial Stage Reactions In Coal Pyrolysis By Molecular Orbital Calculation

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INTRODUCTION

Pyrolysis of coal has been explained based on a chemical percolation and dissociation model [1]. In the early stage of pyrolysis, cross-link structures, which connect aromatic units, as well as peripheral groups, are cleaved, and radical fragments are produced. These radicals are rapidly stabilized to gases, tar and char. The overall pyrolysis reactivity is dependent on the structure of coal.

We recently reported, however, a combination of H₂O₂ oxidation in the presence of alcohols and hydrogenation of the ethanol-extracted samples using a Ru/Al₂O₃ catalyst can alter the coal structure and increase the pyrolysis reactivity. [2] When Yallourn coal was treated by the H₂O₂ oxidation in the presence of alcohols and by the hydrogenation at 120°C for 12-72 h at a hydrogen pressure of 10 MPa, the char yield of flash pyrolysis was decreased from 50wt% for the raw coal to 25wt% for the treated coal [2]. Structural analyses of the hydrogenated coal indicated that aromatic rings of the raw coal were partially converted to saturated rings [3]. This indicates that the coal pyrolysis reactivity is also depended on the unit structure in the coal macromolecule.

In this study, pyrolysis reactivities, as well as product distributions, of raw coals was evaluated using a Curie-point pyrolyzer (CPP). The cleaving energies of unit structures of coal were estimated by a reaction coordinate analysis based on molecular orbital calculation. The coal pyrolysis reactivity was then discussed on the basis of the cleaving energy of unit structures.

EXPERIMENTAL SECTION

Pyrolysis; The elemental composition of the coal is summarized in Table 1. Yallourn (YL), South Banko (SB), Taiheiyu (TH), Miike (MI), and Hunter Valley (HV) coals were ground to give particles which were 37-74 μm in size, and dried at 70°C for 24 h prior to use. A coal sample of 1.5 mg was tightly wrapped with a ferromagnetic foil and pyrolyzed at 386-1040°C using a Curie-point pyrolyzer, which could heat the sample at a heating rate of 3000 K/s. Produced gases were analyzed by GC-TCD and GC-FID. Details of the CPP were reported previously [4].

MO Calculation; The decomposition of unit structures of coals was simulated using WinMOPAC Vr.1 and 2 (Fujitsu), based on a PM3 Hamiltonian and an unrestricted Hartree-Fock method [5]. The unit structure of coal were assumed to be terminated with hydrogen atoms. The molecular weight of the unit structures were 370-398, depending

on coal ranks [6].

RESULTS AND DISCUSSION

Fig.1 shows the snapshots for the detachment of a methoxy group, which is substituted on the unit model structure of a low rank coal (YL). Fig.2 shows the changes in the heat of formation (H.O.F.), corresponding to Fig.1. The distance between the oxygen atom of the methoxy group and the carbon atom of the benzene ring is increased from position with a step of 0.1 Å. The H.O.F., which is E_a at position a, increases with increasing reaction coordinate, and the bond is cleaved at position b. The H.O.F. then approaches to a final value, E_c , when the reaction coordinate is over 2.5 Å [2]. Thus, the energy, which is required to cleave the bond, is calculated from

$$E_{cal} = E_c - E_a \quad (1)$$

where E_c and E_a are the H.O.F at the excited state (position c) and that at the ground state (position a), respectively. Tables 2-4 show the calculated cleaving energies. The numbers in the tables correspond to those in the unit structure models [6]. As shown in Fig.3, the cleaving energies are similar for the coal unit structure models, because the unit structures are not suffered by the effect of non-covalent bond and steric hindrance in the structure. The C=C double bond requires the largest cleaving energy, 420-470 kJ/mol. The cleavage of single bonds on the benzene ring, such as -OH, -Me, and -H groups, needs cleaving energies of 340-410 kJ/mol. This indicates that the elimination of hydroxy and methyl groups and hydrogen from the benzene ring is rather difficult during pyrolysis. However, the elimination of C-C and C-O bonds requires cleaving energies of 170-300 kJ/mol. The cleaving energy of a carboxy group from the benzene ring of the low rank coal is as low as 159 kJ/mol.

The pyrolysis of raw coals was initiated at 350°C, and the coal conversion increased with increasing temperature in the range of 500-800°C. Fig.4 shows the effect of the reaction temperature on the yields from the flash pyrolysis of the YL coal. The temperature effect can be described by the enthalpy, Q_c , which the coal sample attains during the heating from the initial temperature, T_1 , (50°C) to the reaction temperature, T_2 . Assuming that the heat capacity of the coal sample, C_p , is constant in the temperature range, the enthalpy can be described as follows:

$$Q_c = C_p(T - T_1) \quad (2)$$

where Q_c and C_p are expressed based on the mole of carbon in the raw coal. The enthalpy was 6.3-23.3 kJ/mol-C under the present experimental conditions.

As shown in Fig.4, the yield of CO_2 was increased at $Q_c = 8-9$ kJ/mol-C. This is ascribed to the decomposition of carboxy (C-COOH) and methoxy (O-Me) groups. Methylene cross-links (methylene C-C), C-C and C-H single bonds in naphthenic rings (cyc C-C and cyc C-H) may be cleaved in the range of 10-15 kJ/mol-C. The detachment of hydrogen from methyl groups (H-CH₂-) and that of methyl groups (C-Me) also proceeds in this enthalpy range, and the yields of tar and hydrocarbon gases were increased. Double bonds on the aromatic rings (benzene C=C) were cleaved above 450 kJ/mol on the MO calculation, as well as high temperature, whereas the coal conversion was mostly saturated above 20 kJ/mol-C. The coal is then converted to char, which was stable at high temperatures.

Fig.5 shows the yield of total volatile matter, TVM, from pyrolysis of coals of

different ranks. The TVM from the low-rank and subbituminous coals was increased in the range of $Q_c > 10$ kJ/mol-C, and the pyrolysis reactions are ascribed to the decomposition of carboxy and methoxy groups. However, the TVM from the bituminous coals is increased in the range of 10-17 kJ/mol-C and is mostly composed of tar. In this energy range, cross-links were cleaved, and hydrogen was detached, radicals were effectively stabilized by the hydrogen transfer mechanism, and tar was formed. The above experimental results are in agreement with the order of the calculated cleaving energies shown in Fig.3. The pyrolysis reactivity of coal is decided by parallel radical reactions, of which the activation energies are lower than the cleaving energies. Thus, the activation energies for pyrolysis cannot be directly compared to the cleaving energies calculated by the MO calculation. Under the present pyrolysis conditions, however, the pyrolysis reactions occurred in the range of $Q_c = 7-20$ kJ/mol-C. These values are equivalent to approximately 1/20 of the calculated cleaving energies.

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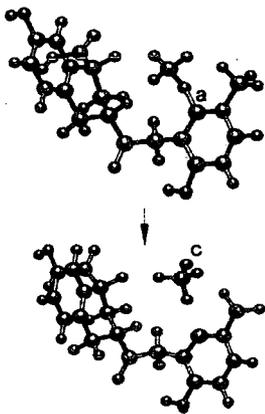


Fig.1 Detachment of a methoxy group from the unit structure model of low rank coal. (Reaction coordinate, a 1.3 Å, c 4.0 Å)

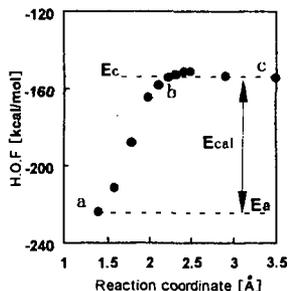


Fig.2 Changes in the heat of formation for detachment of a methoxy group from the unit structure model of low rank coal. Positions a and c correspond to those in Fig.1.

Table 1 Elemental Composition of Coals

coal (abbreviation)	elemental analysis [wt%-daf]				
	C	H	N	(O+S) ^{a)}	ash
Hunter Valley (HV)	80.6	5.5	2.1	11.8	9.5
Miike (MK)	77.9	6.3	1.2	14.6	16.1
Taiheiyō (TH)	73.8	6.6	1.2	18.4	10.9
South Banko (SB)	68.5	5.4	1.2	24.8	2.0
Yalloom (YL)	60.4	5.0	0.5	34.1	1.2

^{a)} determined by reference

Table 2 Cleaving Energies of Bonds in the Unit Structure Model of Low Rank Coal.

bond	position	cleaving energy [kJ/mol]
C-OMe	1	295
O-Me	2	170
C-Me	3	340
C-OH	4	391 - 394
CO-H	5	395
H-C-H	6	295 - 318
benzene-H	7	386 - 416
CO-OH	8	340
C-COOH	9	159
methyleneC-C	10	163 - 320
cycC-C	11	233 - 291
benzeneC=C	12	422 - 474
cycC-H	13	260-306

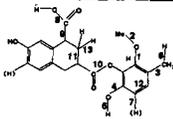


Table 3 Cleaving Energies of Bonds in the Unit Structure Model of Subbituminous Coal.

bond	position	cleaving energy [kJ/mol]
C-Me	1	343
H-CH ₂ -	2	320
C-OH	3	376
H-OC-	4	262
H-CH-	5	257
benzene-H	6	385
C-O	7	189
methyleneC-C	8	227
benzeneC=C	9	448
2benzeneC=C	10	307
2benzeneC=C	11	469

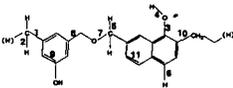


Table 4 Cleaving Energies of Bonds in the Unit Structure Model of Bituminous Coal.

bond	position	cleaving energy [kJ/mol]
C-Me	1	341
C-OH	2	389
H-OC-	3	288
H-CH ₂ -	4	298
benzene-H	5	407
H-CH-	6	279
C-O	7	169
methyleneC-C	8	243
2benzeneC=C	9	457
3benzeneC=C	10	395

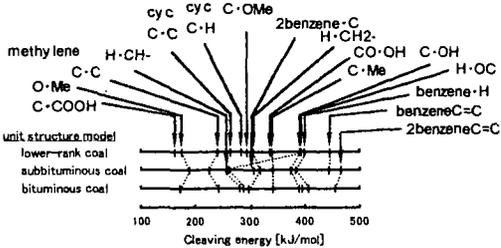
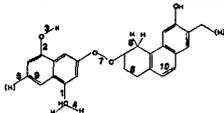


Fig. 3 Cleaving energies for the unit structure models.

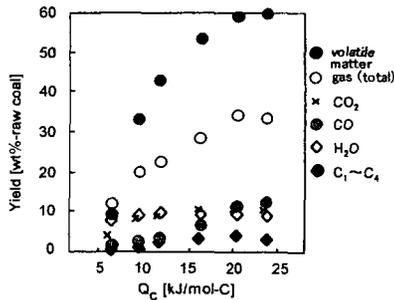


Fig. 4 Effect of enthalpy changes for 1mol of raw coal carbon, Q_c , on product yields by pyrolysis of YL coal.

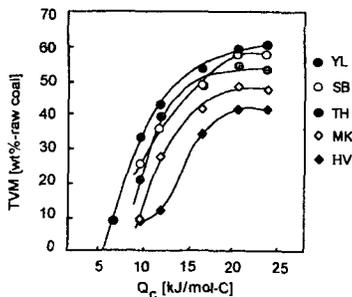


Fig. 5 Effect of enthalpy changes for 1mol of raw coal carbon, Q_c , on the yield of total volatile matter by pyrolysis of coals.