Effects of Pretreatment of Yubari Coal by Solvent-Extraction on the Reductive Alkylation with Molten Potassium and Iodoethane

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Synopsis. Effects of pretreatments of Yubari coal by solvent-extraction on the reductive alkylation with molten potassium and iodoethane have been investigated by comparing the reactions with and without ultrasonic irradiation. Important roles of electron-transfer agents and secondary bonds between coal macromolecules on the anionization were elucidated.

The Sternberg's method of reductive alkylation[1] has been accepted as one of the most effective procedures for the coal solubilization in conventional organic solvents under mild reaction conditions.[2] We have demonstrated previously that highly efficient coal anionization with molten potassium in refluxing tetrahydrofuran (THF)[3] can be further enhanced by ultrasonic irradiation.[4,5] For example, ethylated Yubari coal, prepared by anionization for only 10 min under ultrasonic irradiation, followed by alkylation with iodoethane, yielded 70 wt% of benzene-soluble materials, compared with 41 wt% obtained without ultrasonic irradiation under otherwise the same conditions.[5] Prolonged anionization time both with and without ultrasonic irradiation showed an increase in solubility of alkylated products. Nearly quantitative solubilization in benzene was achieved within 1 h by ultrasonic irradiation but more than 6 h were necessary without the irradiation.[3,5]

In this study, two reactions mentioned above were carried out for the residues of Yubari coal after extraction with different solvents. Such an approach will enable us to assess the role of solvent-extractable constituents in coal on the reactions and to elucidate the reason why ultrasonic irradiation leads to highly efficient reductive alkylation.

Experimental

Pulverized Yubari and Kairan coal samples (−200 mesh) were dried at 110 °C under vacuum overnight. Elemental analyses (dry ash-free basis) are as follows: C, 87.3; H, 6.1; N, 2.0; O (difference), 4.6 wt% for Yubari coal and C, 87.6; H, 4.8; N, 1.5; O (difference), 6.1 wt% for Kairan coal. Extraction solvents (hexane, heptane, chloroform, and benzene) and potassium metal were used as received. Naphthalene used as an electron-transfer agent was purified by recrystallization from ethanol. Purification procedures of THF and iodoethane were described elsewhere.[3–5]

Yubari coal was thoroughly extracted with heptane, chloroform, or benzene using a Soxhlet apparatus for one week. The extract and the residue were dried overnight at 90 °C under vacuum.

A typical reductive alkylation procedure is as follows: a three-necked flask containing THF (50 cm^3) and potassium metal (4 g) was heated in an oil bath until potassium melted and dispersed completely in the refluxing THF. Then, the coal or residue sample (3 g) was added into the flask and agitated by a magnetic stirrer for 6 h under a stream of dry argon. After the anionization of the coal or residue sample with molten potassium, the flask was cooled to 0 °C and then a large excess of iodoethane was added dropwise to the reaction mixture. The resulting mixture was stirred overnight at room temperature.[3] This procedure using molten potassium is called the M-K method. The same procedure was carried out under ultrasonic irradiation by immersing the flask in a heated water bath of an ultrasonic laboratory cleaner (Bransonic B-220, 100 W, 45 kHz, 0.5 W cm^{-2}).[4,5] This procedure under ultrasonic irradiation is called the M-K/US method. Kairan coal sample (3 g) in the presence or absence of naphthalene (0.3 g) was made to react with molten potassium metal (2.4 g) for 2 h under otherwise the same conditions as the M-K and M-K/US methods. It should be mentioned that molten potassium is explosive when exposed to atmosphere. Ethylated products, after repeated washing with deionized water, were subjected to Soxhlet extraction with hexane and benzene for 48 h, and the soluble materials were named Hexane solubles (HS) and Benzene solubles (BS), respectively. Procedures were described in detail elsewhere.[3–5]

The Curie-point pyrolysis of the coal extract (3 mg) was done at 670 °C for 3 s by a pyrolyzer (Japan Analytical Industry Co., model JHP-3). Volatile pyrolysates were analyzed by GLC (Hewlett-Packered, model 5970) and mass spectrometer (JEOL, model DX-303) which were connected to the pyrolyzer, as described in detail elsewhere.[6] The number of ethyl groups per 100 carbon atoms was determined from an increase in weight of the ethylated products.[3]

Results and Discussion

The yield of the extract from Yubari coal increased in the order, heptane (1 wt%) < chloroform (5 wt%) < benzene (12 wt%). The heptane extract showed a high H/C value (1.222) and a low N/C value (0.005), whereas the chloroform extract showed a high N/C value (0.014). In order to characterize the extracts obtained by nonpolar solvents (heptane and benzene), the Curie-point pyrolysis-GC/MS analysis was carried out, indicating that the heptane extract is predominantly composed of long-chain alkanes and that the benzene-extract contains alkylbenzenes in addition to long-chain alkanes. Thus, each extraction solvent (heptane, chloroform, and benzene) may remove aliphatic compounds especially long-chain alkanes, polar compounds containing heteroatoms, and aromatic compounds in addition to heptane solubles, respectively.

Table 1 summarizes properties of Yubari coal, the solvent-extracted residues, and their ethylation products. The properties given are H/C ratio, number of ethyl groups per 100 carbon atoms, and solubility in hexane and benzene (HS and BS, respectively). By the M-K method with molten potassium and iodoethane in THF, ethylated products from the original

Table 1. Properties of Yubari Coal, Residues, and Ethylated Products

Sample	Reaction method[a)]	Atomic H/C	No. of Et added per 100 C[b)]	Solubility/wt%	
				HS[c)]	BS[d)]
Original coal	—	0.84	—	Tr.[e)]	5
Et-product	M-K	1.20	20	36	78
Et-product	M-K/US	1.32	31	60	85
Heptane residue	—	0.84	—	—	—
Et-product	M-K	1.16	14	35	79
Chloroform residue	—	0.82	—	—	—
Et-product	M-K	1.24	19	49	83
Benzene residue	—	0.83	—	—	—
Et-product	M-K	1.02	3	11	63
Et-product	M-K/US	1.20	16	33	83

a) Sample (3 g) was anionized with molten potassium (4 g) using magnetic stirrer (M-K method) or under ultrasonic irradiation (M-K/US method) for 6 h, followed by alkylation with iodoethane. b) Estimated by an increase in weight. c) Hexane-soluble fraction obtained by Soxhlet extraction for 48 h. d) Benzene-soluble fraction obtained by Soxhlet extraction for 48 h. e) Less than 0.5 wt%.

Table 2. Properties of Original and Ethylated Kairan Coals

Sample	Reaction method[a)]	Naphthalene	Atomic H/C	No. of Et added per 100 C[b)]	Solubility/wt%	
					HS[b)]	BS[b)]
Original coal	—	—	0.66	—	2	6
Et-product	M-K	No	0.77	4	6	20
Et-product	M-K	Yes	0.94	12	27	72
Et-product	M-K/US	No	1.05	15	34	75
Et-product	M-K/US	Yes	1.07	18	37	75

a) Kairan coal (3 g) was anionized in the presence or absence of naphthalene (0.3 g) with molten potassium (2.4 g) using magnetic stirrer (M-K method) or under ultrasonic irradiation (M-K/US method) for 2 h, followed by alkylation with iodoethane. b) See Table 1.

coal and the heptane-extracted residue showed a similar solubility in hexane (HS yields were 36 and 35 wt%, respectively) and in benzene (BS yields were 78 and 79 wt%, respectively). The results indicate that long-chain alkanes, which were removed by heptane-extraction, affect little on the reaction. On the other hand, the chloroform-extracted residue gave the product with the highest HS and BS yields (49 and 83 wt%, respectively), whereas the product from the benzene-extracted residue showed the lowest HS and BS yields (11 and 63 wt%, respectively). In contrast, the product from the benzene-extracted residue obtained by the M-K/US method (under ultrasonic irradiation, otherwise the same conditions as the M-K method) sustained rather high HS and BS yields (33 and 83 wt%, respectively), although these values were lower than those of the original coal (60 and 85 wt%, respectively).

The restricted reaction of the benzene-extracted residue by the M-K method (Table 1) may be related to the removal of aromatic compounds from coal by benzene-extraction. In the M-K method, these extracted aromatic compounds may play an important role as electron-transfer agents from molten potassium to bulk constituents in coal. An enhancement of coal anionization with molten potassium in THF in the presence of 18-crown-6, which is known to accelerate the formation of solvated electrons,[7)] suggests the importance of an electron carrier, even for the system with molten potassium. In the case of the M-K/US method, however, the benzene-extractable materials as electron-transfer agents may play a less important role in the anionization reaction (Table 1).

In order to examine the effects of an electron-transfer agent on the coal anionization by both the M-K and M-K/US methods, Kairan coal was subjected to reductive ethylation in the presence and absence of naphthalene as an electron-transfer agent. The results are summarized in Table 2. By the M-K method in the absence of naphthalene, number of ethyl groups added per 100 carbon atoms was 4, and the yields of the HS and BS were 6 and 20 wt%, respectively. By the M-K/US method, number of ethyl groups added (15) and the yields of HS and BS (34 and 75 wt%, respectively) were much higher than those by the M-K method in the absence of naphthalene (Table 2). In the case of the M-K method, however, the presence of naphthalene significantly enhanced the extent of the reaction; The number of ethyl groups added per 100 carbon atoms increased 3 times and the yields of HS and BS increased more than 3.5 times. In contrast, only a small degree of enhancement of the reaction was observed by the M-K/US method. Thus, the results in Table 2 demonstrate that by using the M-K method electron-transfer agents enhance coal anionization with molten potassium compared to the reaction solely with solvated electrons produced in THF. Such acceleration effect of electron-transfer agents has been commonly observed in the reduction of various organic compounds with alkali metal in THF.[8-10] Under ultrasonic irradiation, however, reductive alkylation of Yubari coal in Na/HMPA system has been reported to proceed more efficiently than that in Na/THF/naphthalene system,[11] suggesting that anionization via solvated electrons is more important than that via electron-transfer agents by the M-K/US method.

Since extraction with chloroform was carried out extensively for one week, significant amount of polar compounds, which form secondary bonds (e.g., hydrogen bond) between macromolecules in coal, will be removed for the chloroform-extracted residue. Although THF as the reaction solvent may also remove polar compounds similarly to chloroform, such an effect of THF may be ignored because of much shorter reaction time (6 h) than the Soxhlet extraction with chloroform (one week). The absence of secondary bonds prevents the formation of associated macromolecules to increase mobile constituents in the chloroform-extracted residue[12] compared to the case of the original coal and the heptane-extracted residue, resulting in efficient diffusion of electron-transfer agents to bulk constituents in the residue. This seems to be a reason why the ethylation product from the chloroform-extracted residue shows the highest HS yield among those prepared by the M-K method (Table 1).

The ultrasonic energy adopted in the present study (0.5 $\mathrm{W\,cm^{-2}}$) is reported to be too weak to cleave covalent bonds in coal constituents, but strong enough to destruct secondary bonds between coal constituents.[13] Destruction of such secondary bonds by ultrasonic irradiation may make essentially the same effect as the removal of polar compounds mentioned above. In addition, cavitation induced by ultrasonic irradiation leads to highly efficient diffusion of solvent molecules[14] and presumably of solvated electrons into bulk constituents in coal. This will be the major reason why the M-K/US method leads to the efficient reaction of the benzene-extracted residue as well as the original coal containing polar compounds (Table 1).

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