Solubilization of Meso-Carbon Materials by Butylation with Dibutylzinc and Butyl Iodide

Yan Zhang, Koh Kidena, Satoru Murata, Masakatsu Nomura,* Yoshiharu Yoneyama,† and Tsutomu Kato†
Department of Applied Chemistry, Faculty of Engineeirng, Osaka Universiry, 2-1 Yamada-oka, Suita, Osaka 565
†*Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930*

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Solubilization of meso-carbon microbeads (MCMB) with dibutylzinc-butyl iodide reagents was investigated, this reaction giving tetrahydrofuran-soluble materials in 94-97% yield. This is the first example, to our knowledge, for effective solubilization of these meso-carbon materials. The Mode of introduction of butyl groups was also clarified by using ^{13}C-NMR of butylated samples.

Meso-carbon microbeads (MCMB), prepared from heat treatment of heavy hydrocarbons such as coal tar or pitch, are now used as starting substances for advanced materials like carbon electrodes for lithium ion battery or mechanical seals.[1,2] However, it is too difficult to obtain clear insight into their chemical structures, because these are less soluble in conventional organic solvents and there has been few method for their effective solubilization without destruction of original structure. The structural information is expected to lead more efficient preparation method and/or advanced utilization.

In recent studies,[3,4] we have investigated dibutylzinc-promoted butylation of coal and found that the method is very effective for solubilization of higher rank coals such as Japanese low volatile bituminous Yubari coal (C 87%, daf base), the reaction giving benzene-soluble materials in more than 90% yield. Basic structure of MCMB is believed to consist of polycondensed aromatic clusters, this structural concept being considered to be somewhat similar to that of higher rank coals (higher carbon aromaticity and highly condensed aromatic clusters) except that coal has more aliphatic and oxygen-containing groups than MCMB. Therefore, this solubilization method is expected to be effective for solubilization of MCMB, however, there is few reports for alkylation of these meso-carbon materials.[5] In this paper, we would like to report the results of dibutylzinc-promoted butylation of MCMB samples.

Table 1. Elemental analyses of MCMB and its butylated products

Sample		Elemental analysis / wt% C	H	N	O+S[a]	H/C[b]
MCMB-A	Original	94.2	3.2	1.1	1.5	0.40
	Butylated	88.4	8.5	0.6	2.5	1.14
MCMB-B	Original	94.1	3.3	1.0	1.6	0.41
	Butylated	90.1	8.6	0.5	0.8	1.14

[a] By difference. [b] Atomic Ratio.

Two kinds of MCMB samples employed in this study were prepared from different coal tar pitches,[1] whose carbon aromaticities were different each other. Their elemental analyses are summarized in Table 1. Solubilities of the samples toward quinoline at ambient temperature were less than 10%. We treated MCMB with dibutylzinc-butyl iodide reagents according to the following procedure: A mixture of MCMB (0.5 g), dibutylzinc (10.5 g), and butyl iodide (5 mL) was heated in a 100 mL flask at 180 °C (bath temperature) for 4 h. After the end of the reaction, the remaining dibutylzinc was decomposed in an ice bath by addition of ethanol, then butyl iodide and ethanol being distilled off. The remaining products were washed with diluted hydrochloric acid to remove zinc compounds such as zinc ethoxide or zinc hydroxide, and then washed with water until no halogen ion was detected. Elemental analyses of the butylated samples are shown in Table 1. The resulting butylated MCMB samples (*ca.* 0.5 g) were extracted three times with THF (50 mL) under ultrasonic irradiation. Yields of butylated samples of both MCMB samples were about 170 wt% (based on the weight of each original MCMB sample) and their solubilities reached 94-97%. This is the first example, to our knowledge, for effective solubilization of MCMB. Based on carbon balance, change of H/C atomic ratio, and weight change, we calculated average number of butyl groups introduced, these being 14-17 groups per 100 carbons (Table 2). These introductions should be the origin of a steep increase in solubility of MCMB.

In a previous work, we investigated the alkylation of some coal model compounds like phenanthrene and anthracene with dibutylzinc and butyl iodide reagents.[6,7] Major fashion in the introduction of butyl groups was substitution (non-reductive butylation, product **1**) and addition, these being shown in the following equation. Chemical structure of MCMB is thought to consist of stacked aromatic skeletons. Therefore, addition of alkyl groups (products **2** or **3**) was thought to affect solubility of the butylated products because pendant alkyl groups avoid aromatic-aromatic stacking interactions. Therefore, it is very important what kind of reaction occurred in the alkylation reaction of the MCMB molecules. We measured ^{13}C-NMR of THF-soluble portion of the butylated MCMB-A with a Bruker AC-600 spectrometer in a

Table 2. The results of butylation of the MCMB samples

Sample	Yield of butylated product / wt%[a]	Number of butyl groups introduced / 100C[b] Carbon balance	Atomic ratio	Weight change	Yield of THF soluble product / wt%[c]
MCMB-A	167.5	14.3	16.5	14.9	97.1
MCMB-B	166.9	14.9	16.4	14.7	93.9

[a] Based on the original samples of MCMB. [b] Calculated based on the following three methods such as carbon balance, change of H/C atomic ratio, and sample weight. Details were cited elsewhere. [c] Based on the butylated MCMB samples.

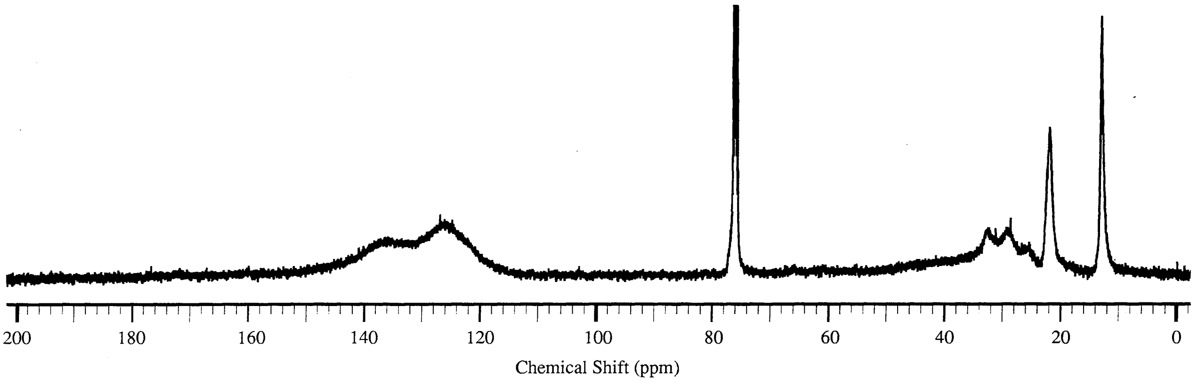
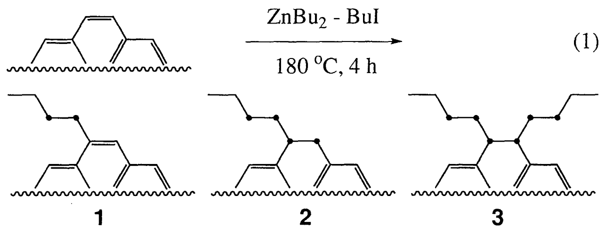
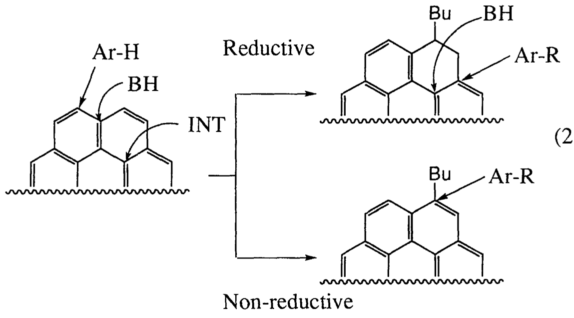


Figure 1. ^{13}C-NMR of THF soluble portion of butylated MCMB-A (gated decoupling method, 7200 scans, 45° pulse, 30sec pulse delay).



(1)



(2)

$CDCl_3$ solution, where almost all the THF soluble portion could be dissolved in $CDCl_3$. In this measurement, the following conditions were employed; gated decoupling method, *ca.* 7200 scans, 45° pulse, and 30sec pulse delay. The resulting spectrum is displayed in Figure 1. Its carbon aromaticity could be calculated to be 0.55. Since the carbon aromaticity of original MCMB was reported to be 0.97-0.98, almost all aliphatic carbons appeared in the spectrum are due to butyl groups introduced and aromatic carbons reduced due to the present butylation reaction. In the aliphatic region of the spectrum, there appeared five peaks or shoulders centered at 13, 22, 26, 29, and 31 ppm. These aliphatic carbons correspond to butyl groups in the type **1**-**3** products (in eq. 1) and reduced aromatic carbons in the type **2** and **3** products. The relative area of the following three regions, 10-18, 18-24, and 24-50 ppm, are found to be 1.0:1.0:2.5, which were assigned as terminal methyl carbons, methylene carbons adjacent to terminal methyl, and the other aliphatic carbons, respectively, according to the chemical shifts reported for alkylbenzenes[8]: Other aliphatic carbons were shown in a filled circled with eq. 1. When substitution reaction occurs predominantly, the ratio should be 1:1:2 (type **1** product), while the ratio of 1:1:4 (type **2** product) or 1:1:3 (type **3** product) should be observed in the addition reaction. The above results might indicate that reductive butylation, *i.e.* addition reaction of butyl groups to the aromatic moieties, contributes to a great extent.

We also investigated the change of the aromatic structures during butylation reaction based on ^{13}C-NMR. In highly condensed polycyclic aromatic compounds, there are four types of carbon (see eq. 2); aromatic carbons bearing hydrogen (Ar-H, 121-132 ppm), internal carbons (INT, 122-129 ppm), bridgehead carbons (BH, 128-136 ppm), and aromatic carbons bearing alkyl group (Ar-R, 135-144 ppm), the numbers in parenthesis indicating chemical shifts of the typical coal model compounds.[8,9] Original MCMB samples showed one broad peak centered at 120-130 ppm in the aromatic region of ^{13}C-NMR, this being assigned as Ar-H, INT, and BH carbons. On the other hand, there are two broad shoulders at around 127 and 137 ppm in the aromatic region of the spectrum of the butylated MCMB. This indicates the increase of BH or Ar-R type carbons. When butyl groups are introduced *via* addition type reaction, Ar-R type carbons should increase, while Ar-H and INT type carbons decrease. On the other hand, in the case of non-reductive butylation (substitution type), amounts of Ar-R and Ar-H change to a small extent, while amounts of INT and BH unchange. These results imply that reductive butylation occurred to some extent in the present butylation reaction and this partly contributed to the higher solubility of the butylated MCMB. We are now investigating detailed analysis of butylated products and conducting the construction of chemical structural model for MCMB molecules.

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