USE OF A1Cl₃-CONTAINING MOLTEN SALTS FOR CARBONIZATION AS SOLVENT AND CATALYST

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ABSTRACT Liquid-phase carbonization was studied using two kinds of molten salts, NaCl 26 –KCl 14 –AlCl₃ 60 mol%(MS-A) and [ethylpyridinium bromide 33 –AlCl₃ 67 mol%(MS-B)], as the reaction solvent and catalyst. As the raw material aromatic compounds such as naphthalene, substituted naphthalenes, anthracene, etc. were mainly used. A raw material dissolved in one of the molten salts was heated at 250 to 300°C for a few to 10 hours yielding coke in the form of powder or flakes. An equimolar mixture of naphthalene with a polychloroethane also gave coke at a temperature as low as 200°C when heated in MS-B. Generally the graphitizability of the resulting cokes ranged widely depending mainly on the nature of the raw material. When stopped halfway, the reaction sometimes yielded a kind of pitch which was easily changeable to mesophase pitch. Some other variations of the procedure and the basic chemistry of these reactions were also studied.

INTRODUCTION

Our study was undertaken in order to gain a better understanding of carbonization in terms of organic chemistry. For this purpose we thought it advantageous to carry out carbonization in solution at least during its earlier stage and decided to employ molten salts as the reaction medium. Here we would like to review briefly our work on a new method of carbon and pitch preparation using two kinds of AlCl₃-rich molten salts. Some researchers have reported on organic reactions using molten salts where tar, pitch, and/or coke were produced. However, these substances have only been regarded as undesirable by-products.

Among many carbon products our interest was focused on recently developed, so-called fine carbons such as carbon fiber, biocarbons, high quality pencil-lead, and so on.
Pitch is an important raw material of carbon, and its characteristics directly determine the properties of the resulting carbon. Therefore, its selection has been one of the most important problems in the production of carbon. Recently its blending and chemical modification have been actively investigated. However, our aim was to obtain the most suitable pitch for the production of a given carbon product by synthesis from pure substances. This process was thought more suitable for the production of fine carbons.

The compositions of our two molten salts, MS-A and MS-B, were as follows:

MS-A (mp. 95°C)
\[\text{AlCl}_3 \text{ 60 mol\% : NaCl 26 mol\% : KCl 14 mol\%}\]

and MS-B (room-temperature molten salt) (1)
\[\text{AlCl}_3 \text{ 67 mol\% : ethylpyridinium bromide 33 mol\%}\].

These molten salts both contain more than 50 mol\% AlCl₃ and, therefore, are strong acids.

Carbonization of low-molecular-weight compounds is a process of polymerization consisting of a very complicated series of reactions. However, these reactions can be classified into two categories. One is the C—C bond formation including the rearrangement. The other is the elimination of elements other than carbon. It was expected that both types of reaction could be catalyzed by a strong acid and that, as a result, the carbonization temperature would be lowered.

1. COKE AND PITCH FROM AROMATICS (2)

One of the molten salts was placed in a glass flask in an argon stream. A raw material was added while being stirred. The mixture was then heated to the desired temperature. Naphthalene and other aromatic compounds were mainly used as the raw material. The quantities of raw material used were 0.05 to 1 in molar ratio to the free AlCl₃. Near the end of reaction a deposition of resulting product was usually observed. After cooling, the reaction mixture was poured into a mixture of ice and diluted hydrochloric acid. The resulting precipitates were filtered, washed, and dried. The crude products were separated by hot-benzene extraction into benzene-soluble (BS) and benzene-insoluble (BI) fractions.

In Table 1 some of the results obtained using MS-A are given, and in Fig.3 the X-ray 002-diffraction profiles
of the coke from naphthalene are given as an example.

Table 1. BIs from Aromatics Obtained by Reactions at 300°C for 10 Hours in MS-A

| No. | Raw material        | Yield (%) | Atomic H/C ratio | X-Ray parameters  |
|-----|---------------------|-----------|------------------|-------------------|
| 1   | Anthracene          | 96        | 0.50             | 3.42, 150         |
| 2   | Phenanthrene        | 71        | 0.48             | 3.37, 700         |
| 3   | Naphthalene         | 92        | 0.47             | 3.37, 700         |
| 4   | 1-Bromonaphthalene  | 98        | 0.40             | 3.40, 200         |
| 5   | 1-Nitronaphthalene  | 99        | 0.35             | 3.52, 20         |

a) After heat-treatment at 2800°C; \(d_{002}\) and \(L_c\) of graphite: 3.354\(\text{Å}\) and 1000\(\text{Å}\), respectively.

In most cases the BIs were a kind of coke. They are insoluble and infusible. The X-ray analysis showed that they had a layer structure which is characteristic of carbon material. These properties and their H/C atomic ratios were very close to those of so-called green coke and carboid coke. We shall call this type of BI "coke" for short hereafter. Quite similar results were obtained when MS-B was used.(3)

Graphitizability is an important property of carbon and it is estimated from the structural parameters measured by X-ray 002-diffraction analysis of a carbon material after a heat-treatment at a temperature usually above 2000°C. The X-ray analysis data, partly given in Table 1 and Fig.3, show that the graphitizabilities of the BIs ranged widely depending mainly on the nature of the raw material; for example, naphthalene gave a highly graphitizable BI, and nitronaphthalene gave a non-graphitizable BI. This indicates that cokes of various graphitizabilities are now available by this method.

Fig.1 shows the photographs of the coke obtained from 1-bromonaphthalene as an example. One can see the thin, wavy film structure.

Some preliminary experiments of carbonization of materials other than aromatics were also examined. Of these, cotton fiber gave the most interesting results (4). It was carbonized by immersing it in MS-B at 150°C for
Monomethylnaphthalenes were isomerized at 100°C - monomethylnaphthalenes were isomerized at 100°C. The reactions were very quick and reached equilibrium within two minutes. The α/β isomer ratio at equilibrium was 4.4. Small amounts of by-products such as naphthalene, dimethylnaphthalenes, tetralin, and polymers were produced. This indicates that, besides the rapid intramolecular α-β migration of methyl groups, intermolecular methyl groups and hydrogen-transfers and polymerization also occurred.

1,2-Dimethylnaphthalene produced isomeric dimethylnaphthalenes and trimethylnaphthalenes when heated in MS-A as shown in Eq. 2. All these products are considered to be the intermolecular rearrangement products because the intramolecular migrations of the methyl groups from 1- to 8-position and from

\[
\begin{align*}
\text{Me} & \quad 100^\circ C, <2\text{min} \quad \xrightarrow{\text{MS-A}} \quad \text{Me} \\
\end{align*}
\]

\[\text{0.7} \quad 107 \quad 4.8\%\]

\[
\begin{align*}
\text{Me} & \quad 100^\circ C, 30\text{min} \quad \xrightarrow{\text{MS-A}} \quad \text{Me} \\
\end{align*}
\]

\[\text{1.2} \quad 12.6\% \quad 3.1\%
\]
1 hour. Unfortunately the resulting carbon fiber was not strong, but improving its mechanical properties seemed possible. When treated similarly with either sulfuric acid or oleum, cotton fiber was destroyed, and the yield was only black powder.

When aromatics were treated under moderate reaction conditions, various pitches were obtained. After separation from the molten salt, the pitches were subjected to an additional heat-treatment. In most of the cases the pitch yielded so-called mesophase pitch.

Fig.2a) and b) are the photographs(5), taken under polarized light, of the pitches obtained from naphthalene by the reaction at 230°C for 5 hours using MS-B followed by an additional simple heat-treatment at 300°C and 400°C, respectively, for 1 hour. The spherical particles appearing in a) are mesophase, and it is reasonably assumed that under a higher heating temperature of 400°C these particles grew larger and unite with each other to a continuous structure of mesophase as shown in b). Such a pitch as easily changing to mesophase pitch at a temperature as low as 300°C was quite new, and is expected to be suitable for producing, e. g., carbon fiber. For comparison Ashland 240 Pitch, a famous commercial product, was also examined similarly, but it did not behave in this way.

The reactivities of the aromatic compounds used were as follows: anthracene > naphthalene > phenanthrene > stilbene > biphenyl > benzene > quinoline. This sequence is similar to those generally observed in electrophilic aromatic substitutions.

Table 2 shows the effect of the composition of molten salt on the BI-yield from anthracene. The use of zinc chloride instead of AlCl₃ made the melt quite inactive. The decreasing AlCl₃-content in the molten salts resulted in decreasing BI-yield. However, it is interesting to see that in the case of No.4 the melt was still active enough to produce an appreciable amount of BI in spite of its AlCl₃-content lower than 50 mol%.

2. ISOMERIZATION, DISPROPORTIONATION, AND POLYMERIZATION OF METHYLNAPHTHALENE(6)

The reactions of mono- and dimethylnaphthalenes in MS-A were studied. Methylnaphthalenes were regarded as simple models of the constituents of tar and pitch.
2- to 3-position are both inhibited.

On the other hand, according to Suld and Stuart(7), the same compound did not react in a superacid of composition of [HF-BF$_3$]. These facts indicate MS-A is a fairly strong superacid. This high acidity is attributable to the combination of the free AlCl$_3$ with HCl generated from the water as contaminant. Furthermore, an addition of a strong protic acid trifluoromethylsulfonic acid accelerated the reaction.

3. CARBONIZATION OF 1,2-DI- and 1,1,2-TRICHLOROETHANE
SUPPLIED IN THE FORM OF VAPOR(8)

Vaporized di- and trichloroethane mixed with a carrier gas of argon were bubbled separately into MS-B at 100, 200, and 300°C yielding cokes although the yields were low. Trichloroethane was more reactive than dichloroethane. The product derived from trichloroethane by the reaction at 300°C was a mixture of a powdery and a film-shaped coke. As given in Fig.4, the latter showed, after heat-treatment at 2500°C, an X-ray 002-diffraction angle 2θ(Kα) of 26.5°, which is practically the same value to that of natural graphite.

4. COKE AND PITCH FROM NAPHTHALENE AND POLYCHLOROALKANES
THROUGH THE FRIEDEL-CRAFTS CO-POLYMERIZATION(9)

According to our view on the nature of carbonization, polymerization deliberately introduced into the earlier stage of carbonization must accelerate the whole reaction, and as a result the carbonization temperature must be lowered. To prove this hypothesis we undertook the following experiments.

Naphthalene was mixed with equimolar amounts of a polychloroalkane in MS-B at room temperature, and the temperature was raised gradually. Interesting results were achieved with polychlorinated methanes and ethanes. The latter's reactions yielded cokes

\[
\begin{align*}
\text{CO-Polymer} & \xrightarrow{-\text{H}_2}\text{Coke} \quad \text{(Eq.3)}
\end{align*}
\]

R: Methylene and Ethylene

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at a temperature as low as 200°C, and when the reactions were stopped at 100°C, the products were pitches.

The experiments showed that in the earlier stage, below 80°C, the main reaction proceeded through the path of the Friedel-Crafts reaction yielding a co-polymer as shown in Eq.3. Following this stage intra- and inter-molecular condensations of the co-polymer took place, accompanied by dehydration, resulting in coke formation.

For comparison naphthalene and dichloroethane were heated to 150°C with AlCl₃ by the standard Friedel-Crafts procedure without molten salt. However, almost no reaction took place. This indicates that the melted salt was essential to these reactions.

Table 3 shows the properties of some of the products. Without chloroalkane only pitch was produced. However, when chloroalkanes were used, the end products were coke. This supports our working hypothesis. The d_{002}-values show that dichloroethane acted to yield non-graphitizable carbon, and trichloroethane, graphitizable carbon. This indicates that we can control the important property of the resulting carbon by adjusting the combination of the raw materials.

Table 3. Products through the Friedel-Crafts Co-polymerization of Naphthalene and Chloroalkanes

| Chloroalkane | Reaction temp. and products | 100°C | 200°C [BI-Content; d_{002}^{a})] |
|--------------|-----------------------------|-------|---------------------------------|
| None         | Tar                         |       | Pitch [53%; 3.39Å]              |
| Cl-CH₂CH₂-C1 | Pitch                       |       | Coke [77%; 3.45Å]               |
| Cl-CH₂CH₂-C1 | Pitch                       |       | Coke [91%; 3.38Å]               |

a) By X-ray 002-diffraction analysis after heat-treatment at 2500°C.

CONCLUSION

Although our study on the chemistry of carbonization is still far from completion, we have already established a new method of making carbon and pitch. The main features of the process can be summarized as follows:
First, the use of this process results in low-temperature carbonization. Second, it consists of solution reactions which proceed through an acid-catalyzed ionic mechanism. Third, it can produce either graphitizable or non-graphitizable carbon, and it can prepare mesophase pitch.

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Fig. 1  a) Coke obtained from 1-bromonaphthalene by the reaction at 300°C for 10 hours in MS-A; b) The same coke photographed with transmitted light. (cf. Sec.1)

Fig. 2  Pitch obtained from naphthalene by the reaction at 230°C for 5 hours in MS-B and following heat-treatment, after separation from MS-B, at a)300°C and b)400°C, respectively, for 1 hour. (cf. Sec.1)
Fig. 3  X-Ray 002-diffraction profiles of BI obtained from naphthalene by the reaction at 300°C for 10 hours in MS-A; a) as obtained, b) after heat-treatment at 2800°C. (cf. Sec.1)

Fig. 4  X-Ray 002-diffraction profiles of two types of BI obtained from 1,1,2-trichloroethane by bubbling it into MS-B at 300°C followed by heat-treatment at 2500°C. (cf. Sec.3)