Characterization of the Nature of De Novo Synthesis by ^{13}C NMR

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Introduction

In 1986 Vogg and Stieglitz first demonstrated the de novo synthesis of PCDD/F: when incinerator fly ash was subjected to thermal treatment at 300°C in air, the PCDD/F content was increased significantly compared to untreated incinerator fly ash [1,2]. Since then many relevant studies have been carried out but the mechanistic details of de novo synthesis remain unclear at present ([3] and references cited therein). Recently it has been observed that de novo synthesis occurs not only in incinerator fly ash but also in particulate matter from pyrometallurgical processes such as copper smelters, so de novo synthesis is probably a basic mechanism of PCDD/F formation common to a number of thermal and pyrometallurgical processes [4]. It is of considerable interest to further investigate the mechanistic details of de novo synthesis.

Solid-state ^{13}C nuclear magnetic resonance (NMR) is a technique useful for characterization of organic structures; aromatic carbon, aliphatic carbon, and carbon bonded to other functional groups can be differentiated in NMR measurements on solid samples. As de novo synthesis involves the interaction of gaseous oxygen with the fly ash matrix, and transformation of solid carbon structures to carbon oxides and organochlorocompounds [3], NMR characterization of solid carbon structures may be helpful for understanding the nature of de novo synthesis. So we attempted NMR measurements on several types of carbonaceous solids.

Material and Methods

The following samples have been tested: (1) Charcoal: sample No. 1 was without any pretreatment; sample No. 2 and 3 were heated at 50 and 80°C for two hours, respectively. After heating, these samples were kept in closed glass bottles until NMR measurement. (2) Activated carbon: NORIT SA3 supplied by NORIT N.V., the Netherlands. Sample No. 1 was without any pretreatment; sample No. 2 and 3 were heated at 50°C for two and four hours, respectively; sample No. 4 and 5 were heated at 80°C for two and four hours, respectively. (3) Incinerator fly ash: sample No. 1 was provided by TNO, the Netherlands; sample No. 2 was provided by Sulzer Chemtech, Switzerland; sample No. 3 was collected from a waste incinerator at Ghent, Belgium.

NMR measurements were done using a Bruker DRX 250 instrument with a magnetic field strength 5.87 T. The solid-state probe used has a spinning speed maximum 5 kHz and can be loaded with about 300 mg sample in the form of a powder. For the charcoal samples ^{13}C NMR measurements

were done with cross polarization and magic-angle spinning (CP/MAS); typical NMR parameters were: repetition time: 4 sec; cross polarization time: 1.5 msec; spinning speed: 4 kHz; total number of pulses: about 2000; total acquisition time: about 2 hours. For the activated carbon samples ^{13}C NMR measurements were done with magic-angle spinning (MAS); typical NMR parameters were: repetition time: 10-20 sec; spinning speed: 3-4 kHz; total number of pulses: 4000-6000; total data acquisition time: about 24 hours.

Results and Discussion

Measurement results for charcoal sample No. 1 and 2 are shown in Fig. 1 and 2, respectively. The aliphatic carbon region is from -20 to 45 ppm and the aromatic carbon region is from 95 to 165 ppm [5,6]. Integration using the appropriate boundaries yields the peak area; dividing the aliphatic peak area by the total peak area gives the aliphatic carbon content which is about 8% for both charcoal samples. The shoulder from 145 to 155 ppm on the high-field side of the aromatic peak is probably from the response of oxygenated aromatic carbon (Ar-O) in phenol, aromatic ether and anhydride [5]. The shoulder shown in Fig. 2 is slightly higher than that in Fig. 1 indicating that more oxygenated aromatic carbon is present in sample No. 2 probably due to oxygen chemisorption during thermal treatment.

The carbon response between 185 to 220 ppm could be from oxygenated carbon in carbonyl, ketone and ester [5]. However, this region is covered by one of the two spinning side bands (SSB) located from 45 to 95 ppm and from 165 to 220 ppm. It is known in NMR [5,6] that SSBs are located symmetrically around the main peak with the distance between SSB and the main peak proportional to the spinning speed, so they can be recognized easily. SSBs arise when the spinning speed is insufficient to overcome the chemical shift anisotropy completely; they can be eliminated by increasing the spinning speed to about 10 kHz. However, this requires the use of a smaller sample weight; and smaller sample weight leads to longer NMR measurement time.

The peak area at the location of an SSB is from a superposition of the true response of carbon nuclei and an SSB; methods are available to substract the SSB and estimate the true response of carbon nuclei, e.g. [7]. For Figs. 1 and 2 if the carbon response at the location of the low-field SSB is neglected, the relative peak area for the low-field SSB is about 0.83. Subtracting the peak area of the low-field SSB from that of the high-field SSB yields: 1 - 0.83 = 0.17 which is the true carbon response between 185 and 220 ppm from oxygenated carbon. Dividing the area of the carbon response from 185 to 220 ppm by the area of the main aromatic peak: 0.17/3.65 = 5%; thus the amount of carbon in carbonyl, ketone and ester is approximately 5% of the amount of aromatic carbon.

NMR measurements for charcoal sample No. 3 and activated carbon samples are similar to those of charcoal sample No. 1 and 2, and are not shown here. However, NMR measurements on incinerator fly ash samples were unsuccessful. In the literature it has been reported that ^{13}C NMR measurements for samples containing a high amount of mineral matter such as iron are very difficult to perform [5,6].

Our measurement results so far have indicated that aromatic carbon and oxygenated functional groups are present in a significant number in carbonaceous solids. A majority of these aromatic carbon-oxygen functional groups can be attributed to the terminating groups in the periphery of a graphitic carbon layer, or oxygen linkages between different graphitic carbon layers, or oxygen heteroatoms within a graphitic carbon sheet. Possibly, the oxygenated functional groups with adjacent aromatic rings are one of the sources of DD/F structures during de novo synthesis; and some of the oxygen in DD/F is from these native macromolecular carbon structures. Previously, Stieglitz et al. [8] tested de novo synthesis using ^{13}C enriched amorphous carbon and observed that PCDF is likely to be formed from biphenyl-like structures in solid carbon. Olie et al. [9] tested de novo synthesis using a mixture of incinerator fly ash and activated carbon in the presence of gaseous $^{18}O_2$, and found that some of the oxygen in PCDD/F originate from the solid carbon structures. Based on these evidence we suppose that de novo synthesis essentially is the oxidative breakdown of macromolecular carbon structures; and PCDD/F arise partially from the aromatic carbon-oxygen functional groups within these macromolecular carbon structures.
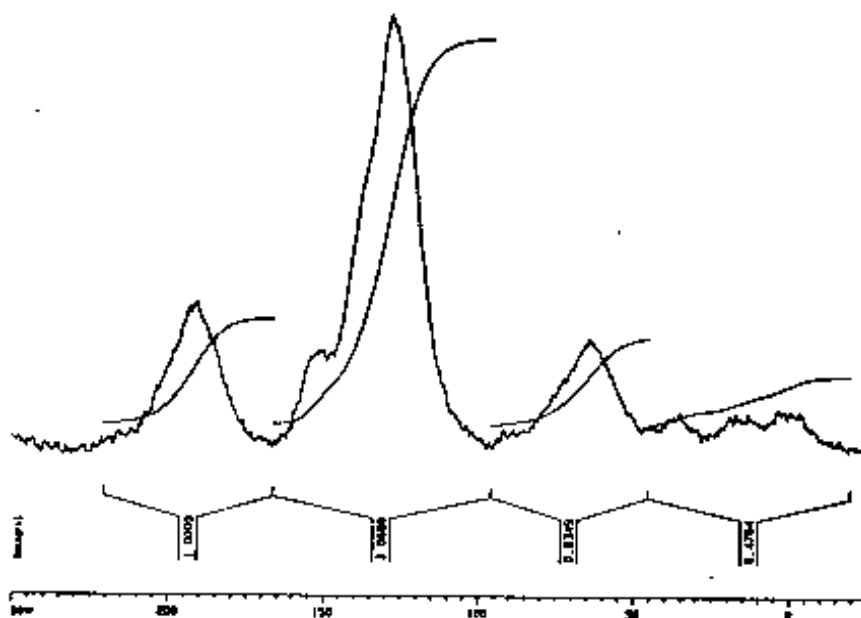

Fig. 1 ^{13}C CP/MAS NMR measurement results for charcoal sample No. 1 (repetition time: 4 sec; cross polarization time: 1.5 msec; spinning speed: 4 kHz; total number of pulses: 2000).
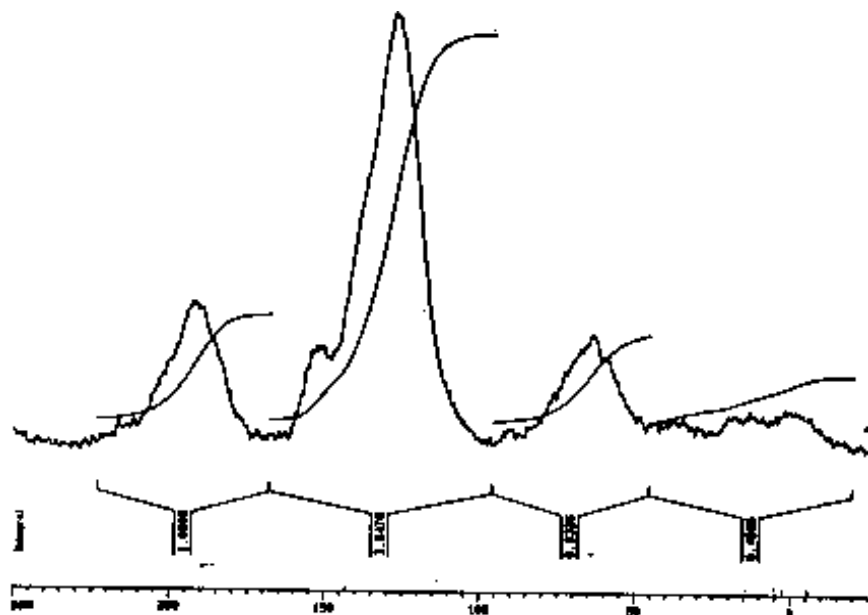
Fig. 2 ^{13}C CP/MAS NMR measurement results for charcoal sample No. 2 (repetition time: 4 sec; cross polarization time: 1.5 msec; spinning speed: 4 kHz; total number of pulses: 1822).

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