

Research Article

Solid-State ^{13}C NMR Spectroscopy Applied to the Study of Carbon Blacks and Carbon Deposits Obtained by Plasma Pyrolysis of Natural Gas

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Solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy was used in this work to analyze the physical and chemical properties of plasma blacks and carbon deposits produced by thermal cracking of natural gas using different types of plasma reactors. In a typical configuration with a double-chamber reactor, N_2 or Ar was injected as plasma working gas in the first chamber and natural gas was injected in the second chamber, inside the arc column. The solid residue was collected at different points throughout the plasma apparatus and analyzed by ^{13}C solid-state NMR spectroscopy, using either cross polarization (CP) or direct polarization (DP), combined with magic angle spinning (MAS). The ^{13}C CP/MAS NMR spectra of a number of plasma blacks produced in the N_2 plasma reactor showed two resonance bands, broadly identified as associated with aromatic and aliphatic groups, with indication of the presence of oxygen- and nitrogen-containing groups in the aliphatic region of the spectrum. In contrast to DP experiments, only a small fraction of ^{13}C nuclei in the plasma blacks are effectively cross-polarized from nearby ^1H nuclei and are thus observed in spectra recorded with CP. ^{13}C NMR spectra are thus useful to distinguish between different types of carbon species in plasma blacks and allow a selective study of groups spatially close to hydrogen in the material.

1. Introduction

Plasma pyrolysis of natural gas is a promising way of producing high-purity carbon blacks without generation of environmentally harmful products. Upon plasma pyrolysis, methane decomposes to produce hydrogen and a solid, carbon-rich residue commonly designed as “plasma black” [1, 2]. These materials are promising for several applications, including the production of inks, electrodes, and catalyst supports [3–5], which means that their profitable use would aggregate value to the process of plasma conversion of natural gas. The detailed understanding of the structure of plasma blacks in the atomic scale is thus of interest aiming their possible practical applications and the optimization of their production methods.

Solid-state ^{13}C nuclear magnetic resonance (NMR) is a spectroscopic method that yields results sensitive to the local atomic environment and which has been used in studies

of carbon materials of diverse types, including peat, humic substances, coal, coke, and chars, among others [6]. In the ^{13}C NMR spectra of these materials, contributions due to aromatic and aliphatic groups are readily separated based on the ^{13}C isotropic chemical shifts, which fall typically between 0 and 90 ppm for aliphatic and in the range 110–160 ppm for aromatic groups. A widespread experimental approach used in solid-state ^{13}C NMR studies of carbon materials involves the use of cross polarization (CP), in order to enhance the polarization of rare ^{13}C nuclei through their interaction with abundant ^1H nuclei, combined to magic angle spinning (MAS). In general, CP experiments are less time-consuming in comparison with experiments based on the direct polarization (DP) of ^{13}C nuclei, since in CP the relevant longitudinal relaxation time is the one associated with the abundant ^1H nuclei ($T_{1\text{H}}$), which is usually much shorter than the ^{13}C spin-lattice relaxation time ($T_{1\text{C}}$). However, the

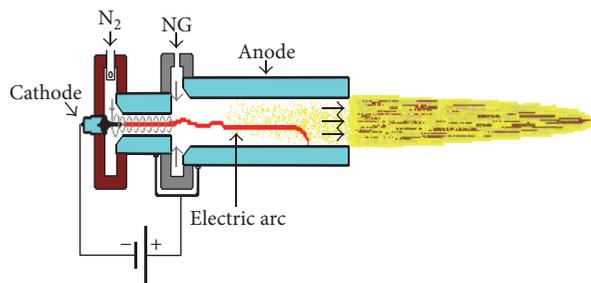


FIGURE 1: Illustration of the plasma reactor used for thermal cracking of natural gas (NG), composed of a double chamber with N_2 as the working gas.

efficiency of CP is strongly dependent on the magnitude of 1H - ^{13}C dipolar coupling, which means that the spectral intensities in a ^{13}C NMR spectrum recorded with CP will be affected by differences in the rate of polarization transfer from 1H to chemically distinct ^{13}C nuclei [6–8]. Also, there are many technologically important types of carbon materials with low (or even zero) hydrogen content, including carbon blacks, carbon nanotubes, nanodiamonds, nanographites, graphene, and amorphous carbon films. For such materials, it is certainly more advantageous to record the ^{13}C NMR spectra using DP, even if these experiments are more time-consuming, allowing a larger portion of carbon atoms to be observed in DP experiments as compared to the CP method. There are plenty of examples in the literature of the successful use of ^{13}C DP/MAS experiments for the analysis of carbon materials, making possible the determination of the fractions of carbon atoms with sp^2 or sp^3 hybridization in carbon films [9, 10], the monitoring of the chemical reduction of graphene oxide [11, 12], the study of the correlation between chemical shifts and structural parameters in heat-treated carbons [13, 14], the study of relaxation processes of ^{13}C nuclei interacting with paramagnetic centers in nanocarbons [15, 16], and many others.

In this work, solid-state ^{13}C NMR spectroscopy was used to study plasma blacks and carbon deposits produced by thermal cracking of natural gas using different types of plasma reactors. The obtained spectra provided a detailed characterization of these materials from the point of view of the local chemical environment of carbon atoms in the material. Both DP and CP approaches were employed, allowing, on the one hand, a thorough characterization of the chemically distinct carbon atomic sites and, on the other hand, the study of minor contributions due to hydrogen-containing groups eventually present in the material.

2. Experimental

The plasma blacks studied in this work were produced as byproducts of the plasma pyrolysis of natural gas (NG). In a typical configuration with a double-chamber reactor (shown in Figure 1), N_2 was injected as plasma working gas in the first chamber and NG was injected in the second chamber, inside the arc column. The double-chamber plasma torches were

composed of a tungsten cathode and a copper step nozzle as the anode. Other plasma gases (e.g., Ar or H_2) were also used in different configurations. The solid residue was collected at different points throughout the reactor. These products were first characterized by thermogravimetry (TG), using a Shimadzu TGA-50H instrument, with constant heating-rate of $20^\circ C/min$ up to $1000^\circ C$ under O_2 flow (50 mL/min); X-ray diffraction (XRD), using a Shimadzu XRD-6000 powder diffractometer operating with a $Cu-K\alpha$ X-ray source (wavelength $\lambda = 1.5418 \text{ \AA}$); scanning electron microscopy (SEM), using a Shimadzu SSX-550 electron microscope; and elemental analysis, performed with a Leco CHNS932 instrument.

Solid-state NMR spectra were recorded at room temperature in a Varian/Agilent spectrometer operating at the NMR frequencies of 399.73 and 100.52 MHz for 1H and ^{13}C nuclei, respectively (magnetic field of 9.4 T), using $^1H \rightarrow ^{13}C$ CP or ^{13}C DP experiments. The carbon-rich powders were mixed with kaolin to avoid problems related to the radiofrequency (RF) penetration in the material (skin depth effect) and to allow a proper tuning of the RF probe [6]. Next, the samples were packed into 4 mm diameter rotors for carrying out MAS experiments, with a spinning rate of 14 kHz. In CP experiments, the duration of the $^1H \pi/2$ pulse was $3.6 \mu s$, the contact time was $500 \mu s$, and the recycle delay was 5.0 s. In the case of DP experiments, a pulse sequence is composed of a $^{13}C \pi/2$ pulse (with $3.3 \mu s$ duration) immediately followed by a pair of π pulses and the subsequent detection of the free induction decay (FID) was employed, in order to suppress spurious background NMR signals coming from some carbon-containing parts of the NMR probe [17]; the recycle delay was 15.0 s in the DP experiments. All spectra were obtained by Fourier transform of the FIDs and the chemical shifts were referenced to tetramethylsilane (TMS), using hexamethylbenzene (HMB) as secondary reference.

3. Results and Discussion

TG and elemental analysis results showed the plasma blacks were primarily composed by carbon, with small amounts of hydrogen (1-2 wt.%) and nitrogen (< 1 wt.%) and reduced ash content (~ 2 wt.%). XRD patterns revealed no crystalline phase, with the detection of only the broad maxima associated with the turbostratic structure typical of disordered carbon materials [18]. SEM images revealed the presence of spherules with varied sizes, typically $< 1 \mu m$, depending on the point of collection of the residue inside the plasma apparatus (see discussion below).

Some typical ^{13}C CP/MAS NMR spectra recorded for plasma blacks produced in N_2 and in Ar plasma reactors are shown in Figure 2. Two resonance bands were clearly observed in the case of the sample produced in the N_2 plasma reactor (Figure 2(a)), broadly identified as coming from aromatic and aliphatic groups. The presence of oxygen- and nitrogen-containing groups is suggested by the chemical shifts observed in the aliphatic region of the spectrum [6]. In the case of the sample produced using the Ar plasma

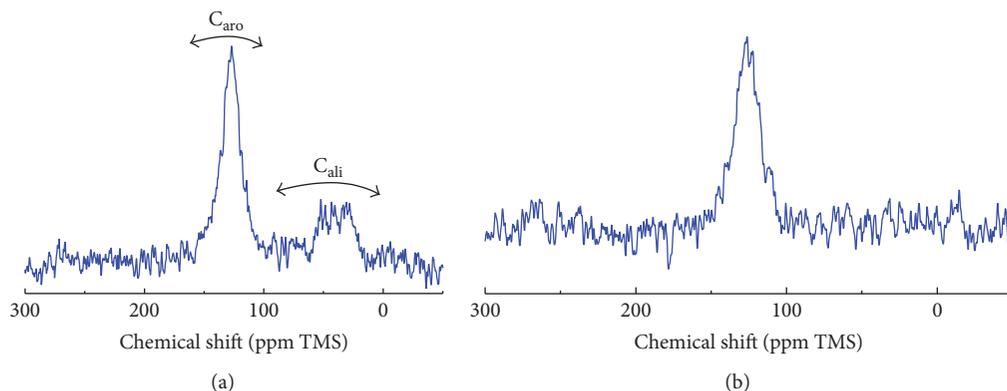


FIGURE 2: ^{13}C CP/MAS NMR spectra of plasma blacks produced by pyrolysis of natural gas in plasma reactors using (a) N_2 or (b) Ar.

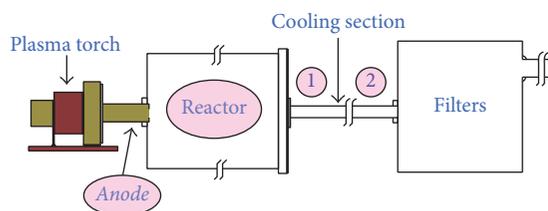


FIGURE 3: Illustration of the apparatus used for Ar plasma reactions; solid residues were collected at four points inside the apparatus: anode, reactor, cooler 1, and cooler 2.

reactor (Figure 2(b)), only an intense aromatic contribution was observed.

As mentioned before, it is worth emphasizing that spectra recorded with CP do not reveal the whole carbon content in the material, being representative only of regions close to hydrogen-containing groups [6, 9, 10, 13]. This is in contrast to what is expected for DP spectra, which contain contributions from essentially all carbon-containing groups. In plasma blacks, with a quite reduced hydrogen content, it is expected that only a small fraction of ^{13}C nuclei are effectively cross-polarized from nearby ^1H nuclei; that is the main reason why the spectra exhibited in Figure 2 present poor signal-to-noise ratio.

In order to establish a detailed comparison between CP and DP NMR spectra of plasma blacks exhibiting different structural features, a set of samples were collected at different points inside the plasma apparatus in an experiment involving the use of Ar plasma for achieving the thermal cracking of natural gas. Figure 3 shows an illustration of the apparatus, with indication of the four points where the solid residues were collected (anode, reactor, cooler 1, and cooler 2). The materials collected at each of these points remained in contact with the hot zone of the plasma torch for different times, so the structural and chemical characteristics of these materials are expected to change from one collection point to another.

Figure 4 shows the SEM images of the materials collected at each of these points. It is clear that the materials collected in the coolers present the smallest particle sizes, with a

morphology similar to what is typically observed for carbon blacks [19, 20]. On the other hand, the materials collected in the main section of the reactor and, especially, inside the anode are composed of larger particles (mostly with diameter $> 1\ \mu\text{m}$), forming agglomerates, which is a consequence of the exposition of these materials to high temperatures for long periods inside the plasma apparatus. The XRD patterns recorded for these samples (shown in Figure 5) reveal the same trends: the widths of the Bragg peaks, particularly the ones corresponding to the (002) peak at $2\theta \cong 26^\circ$, are much smaller for the samples collected in the anode and in the reactor as compared to samples collected in the coolers. This is a further evidence of the better structural order and larger crystallite sizes of the materials that were deposited in the hottest zones of the plasma apparatus.

The ^{13}C CP/MAS and DP/MAS NMR spectra of the samples collected at different points in the Ar plasma apparatus are shown in Figures 6 and 7, respectively. In the case of CP spectra (Figure 6), no NMR signal was obtained for the sample collected in the anode, which is easily explained since the hydrogen content of this sample (also indicated in Figure 6) was below the detection limit of the elemental analysis instrument used in this work. For the other samples, with hydrogen contents around 1 wt.%, CP spectra were successfully recorded, showing the presence of a well-defined resonance associated with aromatic carbons. It is likely that the resonances observed in CP-derived spectra are due to ^{13}C nuclei located at or close to the edges of the graphene-like planes. Being near hydrogen-containing groups, these nuclei are effectively cross-polarized and give rise to the relatively narrow resonances observed with CP.

On the other hand, the DP spectra were effectively observed for all collected samples, including the sample collected in the anode, as shown in Figure 7. The comparison between DP and CP spectra shows that a larger chemical shift range is covered in the DP case, with the resonances observed with the DP method being generally broader in comparison to the corresponding CP spectra. This is a consequence of the fact that in DP experiments the overall carbon content in the material is observed and not only those ^{13}C nuclei close to ^1H nuclei. The resonance peaks in the DP spectra

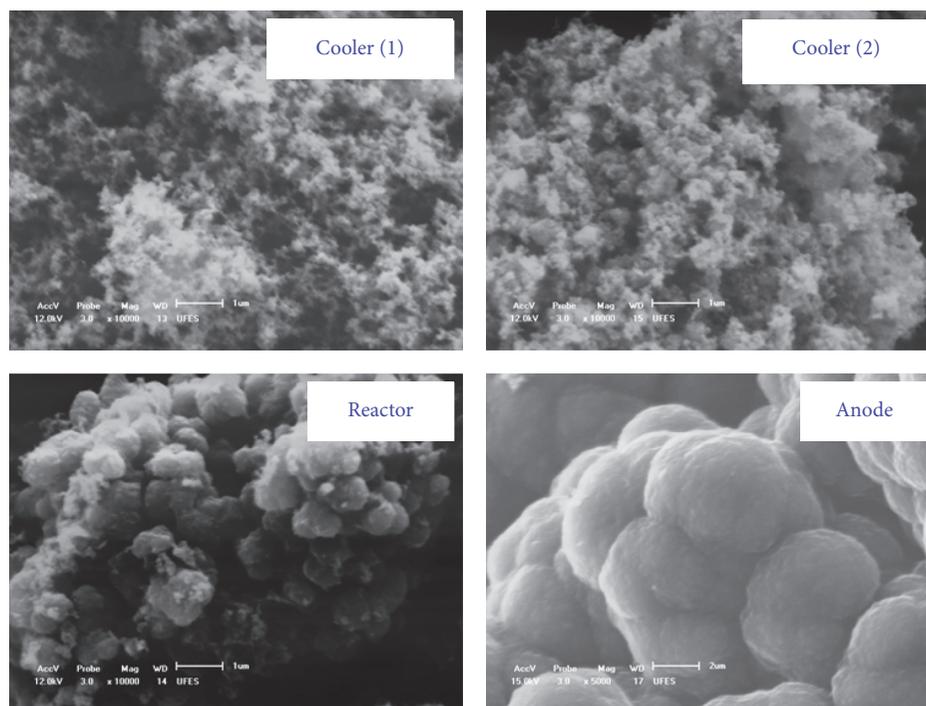


FIGURE 4: SEM images of the carbon residues collected at different points in the Ar plasma apparatus.

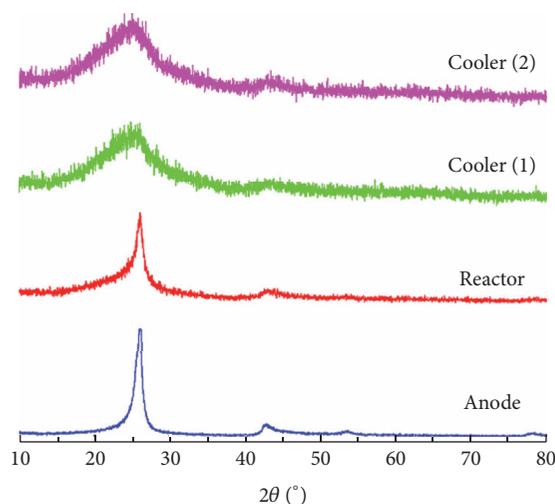


FIGURE 5: XRD patterns recorded for the carbon residues collected at different points in the Ar plasma apparatus.

of the samples collected in the reactor and in the coolers were detected close to 26 ppm, which is a value consistent with the predominantly aromatic character of the material; the corresponding line shapes were found to be similar to the ones observed in carbon materials obtained by the carbonization of organic precursors at high temperatures [13] and also in amorphous carbon films [9, 10].

The large broadening observed in the DP spectra of the carbon residues even when using MAS is attributed to the occurrence of a wide distribution of shifts associated with

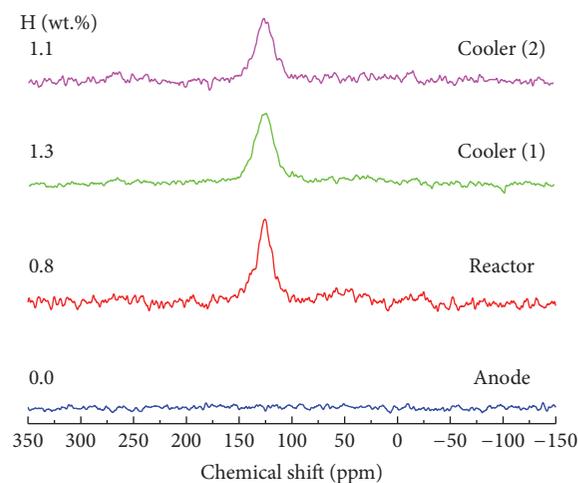


FIGURE 6: ^{13}C CP/MAS NMR spectra of the carbon residues collected at different points in the Ar plasma apparatus. The hydrogen contents of each sample (obtained by elemental analysis) are also informed.

the locally anisotropic magnetic susceptibility of graphene-like planes [14]. Thus, the extent of this broadening and also the peak position are expected to reveal details about structural aspects of the material. The existence of graphene-like planes arranged in the turbostratic structure within the spherules observed in the SEM images is thus related to the large broadening observed in the ^{13}C NMR spectra of the analyzed samples. The observation of a large broadening and a sizeable upfield shift for the resonance peak in the

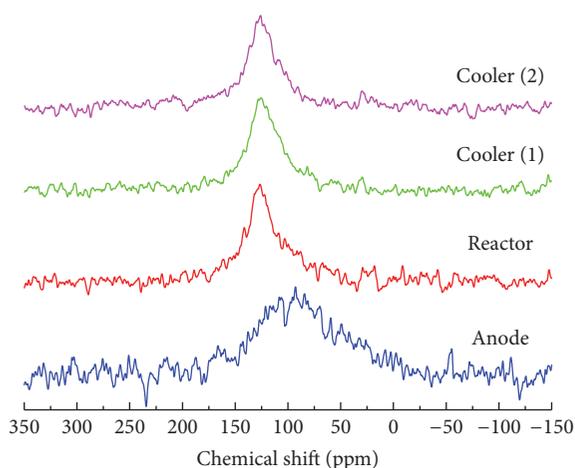


FIGURE 7: ^{13}C DP/MAS NMR spectra of the carbon residues collected at different points in the Ar plasma apparatus.

^{13}C DP/MAS NMR spectrum of the sample collected inside the anode is particularly remarkable (Figure 7). The peak position was found close to 90 ppm, which is a value quite low in comparison to the typical chemical shift range of sp^2 carbons [6], but is similar to what has been observed in graphite samples [14, 21]. This large upfield shift and the severe broadening of this resonance are effects associated with the improved structural organization of this material, as also revealed by the SEM and XRD results previously discussed, which is a consequence of the long residence time of this material in the high-temperature region inside the anode. Thus, this sample exhibits structural features very distinct from the other ones, leading to the resemblance of the corresponding NMR spectrum to the spectra commonly observed for graphitic materials [14, 21].

A scenario similar to the one described here has been reported in the NMR analyses of hydrogenated amorphous carbon films, where the comparison between CP and DP spectra has allowed the distinction between sp^2 - and sp^3 -like carbon atoms [9, 10]. In these materials, the ^{13}C CP/MAS NMR spectra are representative of just a part of the carbon network, but, given the improved sensitivity of CP experiments compared to DP ones, it is possible to detect even minor contributions associated with hydrogen-containing chemical groups. As an example, Pan et al. [9] estimated that the CP/MAS spectrum recorded for an amorphous carbon film represented only 1.5% of the total amount of carbon atoms in the material, with the spectrum indicating the presence of both sp^2 - and sp^3 -like contributions. In a related work, Cho et al. [10] used a combination of DP/MAS and CP/MAS spectra to study amorphous hydrogenated carbon films prepared by sputtering. The DP/MAS spectra were employed to achieve information on the total contents of sp^2 - and sp^3 -like groups; on the other hand, the CP/MAS spectra recorded with spectral editing methods allowed the assessment of the chemical changes occurring in films with different hydrogen contents. The analysis of the ^{13}C NMR spectra of the plasma blacks and carbon deposits described

here allows a similar assessment of contributions from carbon atoms located far within the graphene-like planes or those located close to the plane edges and thus more susceptible to the polarization transfer from nearby ^1H nuclei present in functional groups.

4. Conclusion

This work shows how solid-state ^{13}C NMR spectroscopy methods can be useful to distinguish between different types of carbon-containing groups and to allow a selective study of groups spatially close to hydrogen in carbon blacks and carbon deposits obtained by plasma pyrolysis of natural gas. For samples collected at different points along the plasma apparatus, the results evidenced a good correlation between the structural features (revealed by XRD and SEM) and the spectral characteristics observed in the ^{13}C DP/MAS NMR spectra. Even with little hydrogen content in the plasma blacks and in the deposited carbon residues, the combination of CP and DP methods allowed the detection of signals coming from carbon atoms close to hydrogen-containing groups at the plane edges and also from carbon atoms located far within the graphene-like planes.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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