

Tow Solid-state ^{13}C Nuclear Magnetic Resonance Methods for Detecting Chemical Structure of Coal Combustion Emissions

ZHANG Xiang Yun^{1, 2, a*}, LI Jun^{1, b}, Mo Yang Zhi^{1, 2, c}, ZHANG Gan^{1, d}

¹ State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

² University of Chinese Academy of Sciences, Beijing 100049, China

^{a*} email: zhangxiangyun@gig.ac.cn, ^bemail: junli@gig.ac.cn, ^cemail: moyangzhi@gig.ac.cn, ^demail: zhanggan@gig.ac.cn

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Abstract. This work introduces tow solid-state ^{13}C Nuclear Magnetic Resonance (NMR) methods, cross polarization- total suppression of sidebands/magic angle spinning (CP-TOSS/MAS) and direct polarization/magic angle spinning (DP/MAS), for detecting chemical structure of coal combustion emissions. The CP-TOSS/MAS NMR experiment result of the standard sample overestimate the value of $\text{sp}^3\text{-C}$ group ($25\pm 5\%$). This is also demonstrated in the Pingdingshan coal combustion emissions sample. DP/MAS NMR is more accurate in detecting the structure of compounds, but this method need much more time.

Introduction

Carbonaceous particles, which contribute 10–70% to the atmospheric fine particulate matter, [1,2] are of worldwide concern due to their effects on climate and human health. [3,4] The complex content of carbonaceous particles (total carbon, TC) derives from incomplete combustion of fossil fuels (coal and petroleum) or biomass [5]. Complexity and insolubility of carbonaceous particles have presented a big challenge in its characterization. Among the various analytical methods applied to carbonaceous particles characterization, nuclear magnetic resonance (NMR) spectroscopy becomes increasingly the method of choice due to its capacity to provide comprehensive structural information nondestructively [6].

Nuclear magnetic resonance (NMR) spectroscopy relies on the absorption (i.e. resonance) of radio frequency (rf) energy by nuclei. While the magnetic moment of a nucleus (e.g. ^1H) is constant, their location in a compound regulates the amount of absorbed rf energy to achieve resonance, which in turn, is related to the strength of the secondary magnetic field generated by the movement of electrons within the external magnetic field. The resonances of individual nuclei are reported in relation to a signal of a chemically nonreactive reference compound such as tetramethylsilane ($(\text{CH}_3)_4\text{Si}$) [7]. The versatility of NMR spectroscopy has made it a widespread tool in chemistry for the study of chemical structure [8, 9]. And the researchers also have made a series of research results on the study of humic acid, black carbon and water soluble organic carbon of the atmospheric aerosol by NMR technology [10-14]. The solid-state ^{13}C NMR spectroscopy has been extensively adopted to obtain the quantitative structural information on coal carbonaceous [15]. But ^{13}C NMR data of coal combustion emissions is rarely reported. This paper introduces tow solid-state ^{13}C NMR methods (CP-TOSS/MAS and DP/MAS) for detecting chemical structure of coal combustion emissions.

Experimental

Samples. Coal combustion emissions were collected from Pingdingshan coal with high-volume samplers (XT-1025, Shanghai XTrust Analysis Instrument and Technology Co., Ltd.). The standard sample is glycine (Sigma, USA).

NMR Spectroscopy. All the experiments were performed using a Bruker AVANCE III 400 MHz NMR spectrometer. The resonance frequency of ^{13}C is 100.613/MHz, with a standard glycine for chemical shift calibration. And NMR experiments were run using a Bruker 4 mm double-resonance probe head and a ZrO_2 rotor. The data was processed with Bruker.Topspin3.1 software.

CP-TOSS/MAS spectra, with the pulse sequence of Figure 1, were run at a spinning speed of 5 kHz. In the pulse sequence, four 90° pulses total suppression of sidebands (TOSS) was employed before detection. This method can reduce the peak area of sideband to less than 5% [16]. The acquisition time is 5.12 μs , and the spectral width is 100 kHz. The 90° ^{13}C pulse length was 11 μs and the recycle delay time is 1s.

DP/MAS spectra, with the pulse sequence of Figure 2, were run at a spinning speed of 14 kHz. Pulse sequence for quantitative ^{13}C DP/MAS NMR, consisting of a 90° pulse for excitation and a 180° pulse after a rotation period t_r , to form a Hahn echo at $2t_r$, which avoids baseline problems due to probe head dead time [17]. The acquisition time is 5.12 μs , and the spectral width is 100 kHz. The 90° ^{13}C pulse length is 4 μs . The 180° ^{13}C pulse length is 8 μs . The recycle delay for DP/MAS ^{13}C NMR of the sample based on CP/T1/TOSS experiments [17].

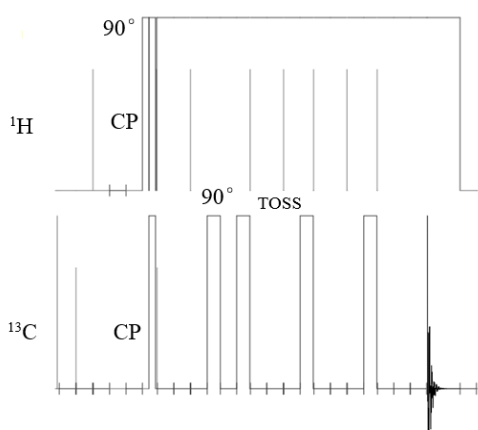


Fig1. Pulse sequence of CP-TOSS/MAS NMR

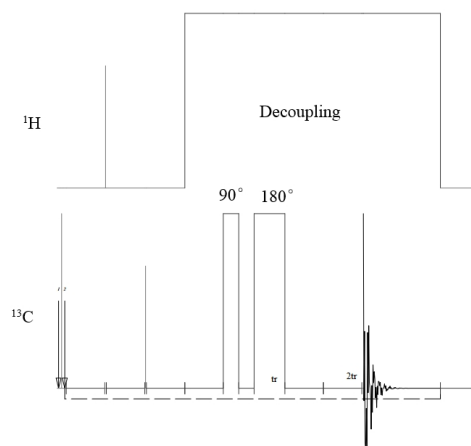


Fig2. Pulse sequence of DP/MAS NMR

Results and discussion

Demonstration on standard sample. Fig. 3 shows the NMR spectra of glycine from CP-TOSS/MAS experiment, with the pulse sequences of Fig. 1 at 5 kHz, and scan numbers from 10 to 128. And Fig. 4 displays the NMR spectra of Glycine from DP/MAS experiments, with the pulse sequences of Fig. 2 at 14 kHz, and scan numbers from 8 to 100. Fig.3 shows that the sideband becomes large with the increase of the number of scan. And the ratio of CH_2 (sp^3) to COOH is 1.25 ± 0.05 . That means CP-TOSS/MAS experiment method overestimate the value of CH_2 (sp^3) group ($25 \pm 5\%$). For this aspect, DP/MAS NMR is much more accurate. The ratio of CH_2 to COOH is 1 ± 0.05 from the Fig. 4. But DP/MAS NMR experiment method need much more time. The recycle delay for DP/MAS ^{13}C NMR of glycine was chosen as 25s, which based on CP/T1/TOSS experiments [17].

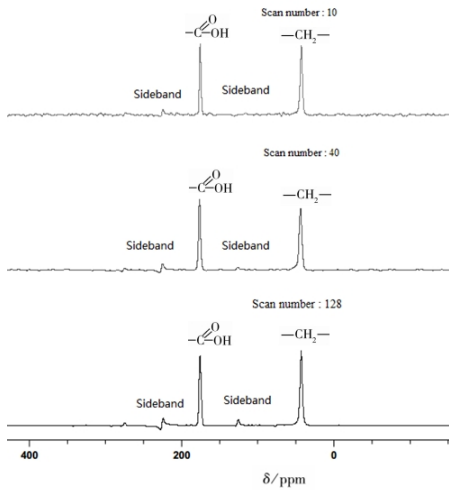


Fig3. The NMR spectra of Glycine from CP-TOSS/MAS experiments

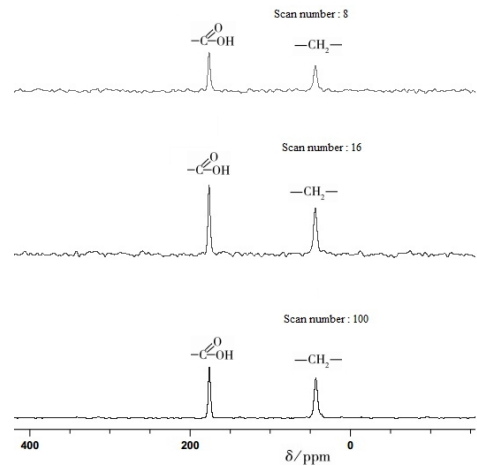


Fig4. The NMR spectra of Glycine from DP/MAS experiments

Application to coal combustion emissions with CP-TOSS/MAS NMR and DP/MAS NMR methods. The pretreatment method of Pingdingshan coal combustion emissions sample is referring to our previous work [16]. Fig. 5 displays this sample's NMR spectra obtained with the CP-TOSS/MAS NMR and DP/MAS methods, respectively. The scan number of CP-TOSS/MAS experiment is 2448, with the pulse sequences of Fig. 1 at 5 kHz. And the scan number of DP/MAS experiments is 4206, with the pulse sequences of Fig. 2 at 14 kHz. The recycle delay for DP/MAS ¹³C NMR of coal combustion emissions was chosen as 20 s, based on CP/T1/TOSS experiments [17]. The value of sp³-C with the CP-TOSS/MAS experiment overestimate 28.33% ((44.93-35.01)/35.01) compared with the DP /MAS experiment from the table 1. The data processing method is referring to our previous work [16].

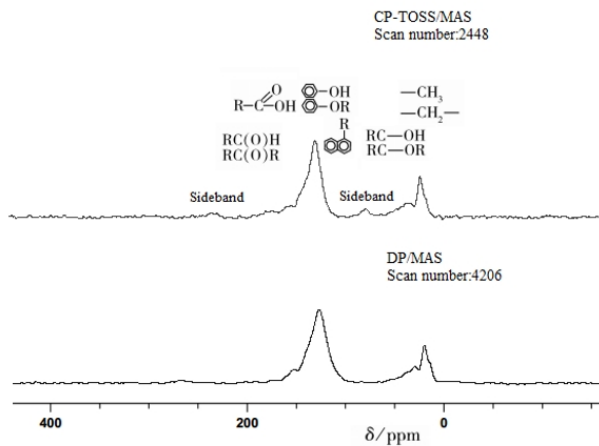


Fig5. The NMR spectra of Pingdingshan coal combustion emissions from CP-TOSS/MAS and DP/MAS experiments

Table.1 Variations of carbonaceous component in Pingdingshan coal combustion emissions by CP-TOSS/MAS and DP/MAS NMR methods

NMR method	sp-C and sp ² -C %	sp ³ -C %	sp ³ -C/sp ³ -C and sp ² -C %
CP-TOSS/MAS	66.93	30.07	44.93
DP/MAS	74.07	25.93	35.01

Conclusion

Tow NMR technique for detecting chemical structure of coal combustion emissions, has been demonstrated on both standard sample and Pingdingshan coal combustion emissions. The CP-TOSS/MAS experiment result of the standard sample overestimate the value of sp³-C group (25±5%). This is also demonstrated in the Pingdingshan coal combustion emissions sample. The DP/MAS NMR is much more accurate, but it needs much more time. Therefore, the DP/MAS NMR is better for the accurate detection of structure. However, if there are a lot of samples or the purpose is the changing trend, the CP-TOSS/MAS NMR is better than the DP/MAS NMR.

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References

- [1] H. J. Lim, B. J. Turpin: Environ. Sci. Technol. Forum Vol. 36 (2002), p. 4489-4496
- [2] G. Lonati, S. Ozgen, M. Giugliano: Atmos. Environ. Forum Vol. 41 (2007), p. 4599-4610
- [3] J. L. Mauderly, J. C. Chow: Inhalation Toxicol. Forum Vol. 20 (2008), p. 257-288
- [4] E. J. Highwood, R. P. Kinnersley: Environ. Int. Forum Vol. 32 (2006), p. 560-566
- [5] S. Fuzzi, M. O. Andreae, B. J. Huebert, et al: Atmos. Chem. Phys. Forum Vol. 6 (2006), p. 2017-2038
- [6] B. J. Turpin, P. Saxena, E. Andrews: Atmos. Environ. Forum Vol. 34 (2000), p. 2983-3013.
- [7] Marie-Cecile G. Chalbot, Ilias G. Kavouras: Environmental Pollution. Forum Vol. 191 (2014), p. 232-249
- [8] Q. G. Tan, X. D. Luo: Chem. Rev. Forum Vol. 111 (2011), p. 7437-7522
- [9] Z.Y. Zhou, J. K. Liu: Natural Product Reports. Forum Vol. 27 (2010), p. 1531-1570
- [10] S. Decesaria, M. C. Facchini, S. Fuzzi, G. B. McFiggans, H. Coe, K. N. Bower: Atmospheric Environment. Forum Vol. 39 (2005), p. 211-222
- [11] Y. C. Li, J. Z. Yu, S. S. H. Ho, Z. B. Yuan, A. K. H. Lau, X. F. Huang: Atmospheric Research. Forum Vol. 118 (2012), p. 41-51
- [12] E. Tagliavini, F. Moretti, S. Decesari, M. C. Facchini, S. Fuzzi, W. Maenhaut: Atmospheric Chemistry and Physics. Forum Vol. 6 (2006), p. 1003-1019
- [13] L. D. Ziemba, R. J. Griffin, S. Whitlow, R. W. Talbot: Atmospheric Environment. Forum Vol. 45 (2011), p. 7319-7329
- [14] M. C. Chalbot, G. Nikolich, V. Etyemezian, D. W. Dubois, J. King, D. Shafer, G. Gamboa da Costa, J. F. Hinton, I. G. Kavouras: Environmental Pollution. Forum Vol. 181 (2013), p. 167-171
- [15] M. S. Solum, R. J. Pugmire, D. M. Grant: Energy Fuels. Forum Vol. 3 (1989), p. 187-193
- [16] X. Y. Zhang, J. Li, D. Liu, K. J. Shen, G. Zhang: J. Instrum. Anal. Forum Vol. 34 (2015), p. 856-859
- [17] J. D. Mao, K. Schmidt-Rohr: Environ. Sci. Technol. Forum Vol. 38 (2004), p. 2680-2684