

Solid-state ^{13}C NMR studies of activated carbons prepared from biomass using different chemical agents

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Introduction

Activated carbons are largely employed in several chemical and physical processes nowadays, including water treatment, catalysis, gas storage and others [1]. The surface properties of the porous carbons are determinant for most of such applications. Oxygenated functional groups present at the edges of the aromatic lamellae are known to influence decisively the surface chemistry of these materials [2]. In this work, solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy was used for the analysis of a series of activated carbons prepared from a lignocellulosic precursor, using different chemical activating agents.

The lignocellulosic precursor chosen for the preparation of the activated carbons was the testa of *Mesua ferrea* oil seed, which is found extensively in North East India and is used in the production of biodiesel. The precursor, after water washing and drying, was cut into small pieces and carbonized at 450°C for 30 min under N_2 flow. From this resulting char, activated carbons were prepared by chemical activation with KOH, NaOH, CaCl_2 or H_3PO_4 , using an impregnation procedure. The activation heat-treatments were carried out at different final temperatures (in the range 500-950°C) under N_2 flow. Some samples were prepared by carbonization of the precursor without any activating agent, for comparison. The products were initially washed repeatedly with hot distilled water. Some selected samples were also washed by refluxing with 25% HNO_3 for 2h at the water boiling point and then filtered and washed again with hot distilled water for several times. Finally, all samples were washed with methanol and then dried at 110°C for 48h.

Solid-state NMR spectra were recorded at room temperature using two NMR spectrometers. Experiments with ^1H - ^{13}C cross-

polarization (CP) were conducted in a Varian INOVA 400 spectrometer at a frequency of 100.5 MHz (magnetic field of 9.4 T), whereas single pulse excitation (SPE) experiments were performed using a Chemagnetics-Varian 200 spectrometer at 51.4 MHz (4.7 T). The chemical shifts were externally referred to tetramethylsilane (TMS). All experiments were conducted with magic angle spinning (MAS). Recycle delays varied in the range 1-10 s, being adjusted to avoid saturation problems.

Results and Discussions

The ^{13}C SPE-MAS NMR spectra of a set of activated carbons are shown in Fig. 1, compared to the spectrum corresponding to the precursor charred at 850°C. All spectra are dominated by a broad and intense band associated with aromatic carbons. Weak aliphatic contributions can be observed in some spectra, especially for the non-activated char.

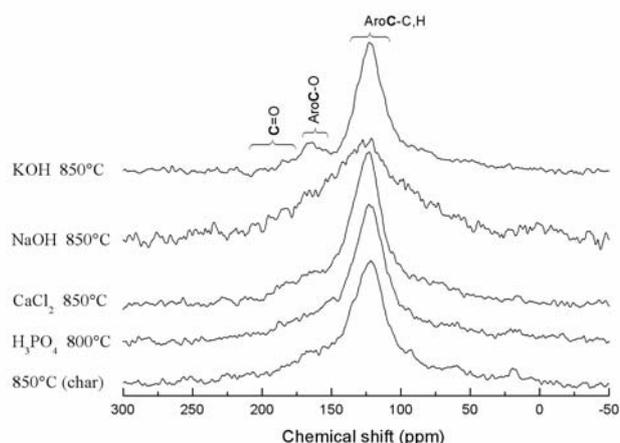


Figure 1. ^{13}C SPE-MAS NMR spectra of the charred precursor and a set of activated carbons prepared with different chemical agents.

The presence of resonances due to oxygenated functional groups is observed in the range 160-210 ppm. These groups are especially visible for the KOH-activated sample.

A strong intensity in this chemical shift range is also observed in the spectrum corresponding to the NaOH-activated sample, but the excessive broadening of the resonances precludes a precise assignment in this case. This finding is likely to be associated with the dipolar coupling between the ^{13}C nuclei and the quadrupolar and abundant ^{23}Na nuclei in the neighborhood [3].

The ^{13}C SPE-MAS NMR spectra of the activated carbons prepared with H_3PO_4 as the activating agent at different temperatures are shown in Fig. 2. The spectrum corresponding to the non-activated char, also shown in Fig. 2 for comparison, shows the presence of a sizeable aliphatic contribution around 25 ppm. All activated samples are predominantly aromatic.

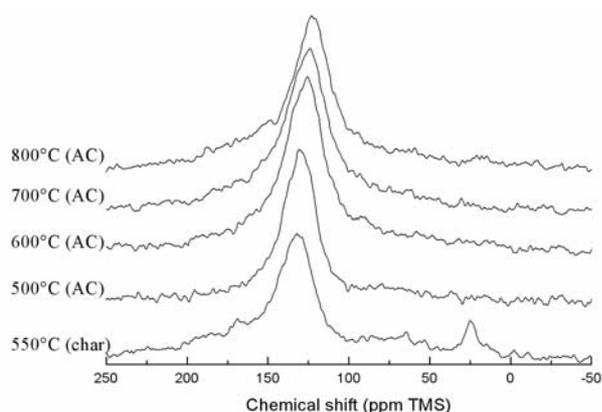


Figure 2. ^{13}C SPE-MAS NMR of the charred precursor and the activated carbons (AC) prepared at different activation temperatures using H_3PO_4 as the activating agent.

The chemical shift of the strong aromatic peak decreases with the increase in the activation temperature, as a consequence of the increase in the diamagnetic susceptibility of the graphene-like planes [4]. It is interesting to mention that this trend is also observed for the

chemical shifts of the main resonance found in the ^{31}P NMR spectra (not shown), which indicates the proximity of the phosphorous species and the aromatic planes in the H_3PO_4^- activated carbons.

Conclusions

Solid-state ^{13}C NMR was used to study a series of activated carbons prepared from different chemical activating agents. The predominantly aromatic nature of all activated materials was clearly established. Oxygenated functional groups were detected especially for the alkali-activated carbons. For samples prepared at different temperatures, the chemical shift of the aromatic resonance showed a trend of reduction with the increase in the activation temperature, caused by the increase in the diamagnetic susceptibility of the graphene-like planes in the activated carbons.

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¹ Marsh, H.; Rodriguez-Reinoso F. 2005. *Activated Carbon*. Elsevier, Amsterdam.

² Leon y Leon, C. A.; Radovic, L. R. 1994. *In: Chemistry and physics of carbon*, vol. 24, P. A. Throver (editor), Marcel Dekker, New York, pp. 213-310.

³ Duer, M. J. 2004. *Introduction to Solid-State NMR Spectroscopy*. Blackwell, Oxford.

⁴ Freitas, J. C. C.; Emmerich, F. G.; Cernicchiaro, G. R. C.; Sampaio, L. C.; Bonagamba, T. J. 2001. *Solid State Nucl. Magn. Reson.* 20, 61-73.