

¹³C MAS NMR AND XPS CHARACTERIZATION OF NITROGEN-MODIFIED CARBONS

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Introduction

The significance of the surface chemistry of activated carbon in catalysis becomes increasingly apparent. Detailed studies have mostly been centered on oxygen-containing functional groups. This is obvious, as oxygen is naturally present in reasonable amounts and functional groups containing oxygen can be studied with relative ease compared to those containing *e.g.* nitrogen. Nitrogen introduced to carbon, however, led to a number of interesting effects, which for some part appeared to be hard to explain. This difficulty may well be related to the insufficient level of knowledge of the surface chemistry of nitrogen-containing functional groups on carbons[1]. The potential of these materials is largely uncovered, but apparently nitrogen containing carbons promise to be good solid basic catalysts[1] and, as catalyst supports, bind heteropoly anions very strongly[1].

Exploring the surface chemistry of nitrogen on carbon surfaces, first amination and ammoxidation (treatments of carbon with ammonia) were studied. The engineering of the chemistry of nitrogen by heat treatment between 200 and 1000°C was studied in detail[2]. Below 350°C amides, imides and lactams are believed to form, which are gradually converted to pyridines and pyrroles, up till 800°C. Around 900°C about half of the aromatic nitrogen functions are decomposed with HCN evolution.

Organic amines, chemically attached to commercially available activated carbons via spacing groups[3], are presently studied with ¹³C MAS NMR. The results are reported and compared with a recent XPS-study[4]. Comparison of the NMR spectrum of the newly modified carbon with those of model compounds allowed unequivocal determination of the structure of the nitrogen-containing surface groups. Comparison of the XPS spectra of the new carbon modifications with those of the aminated and ammoxidated carbons may then confirm the existence of the assumed amide, imide and lactam functional groups[2]. Supporting characterizations included FTIR spectroscopy, acid/base titration and elemental analysis.

Experimental

The organic amine modified carbons were prepared by reaction of oxidized carbon with amines via two routes. The carbon coded C is a granular, chemically activated carbon and the carbon coded R is an 0.8x5mm extruded, gas activated carbon (courtesy of Norit NV, the Netherlands). C and R were oxidized by boiling in 30wt.% nitric acid during 3hours[5]. The amines, N,N-dimethyl-1,3-propanediamine (dmpa) and N,N-dimethylethanolamine (dmea), were attached to the carbons by a **low-T-route** (<65°C), in this case first a treatment of the carbons with thionyl chloride was applied, and by a straightforward **high-T-route** (133°C)[3].

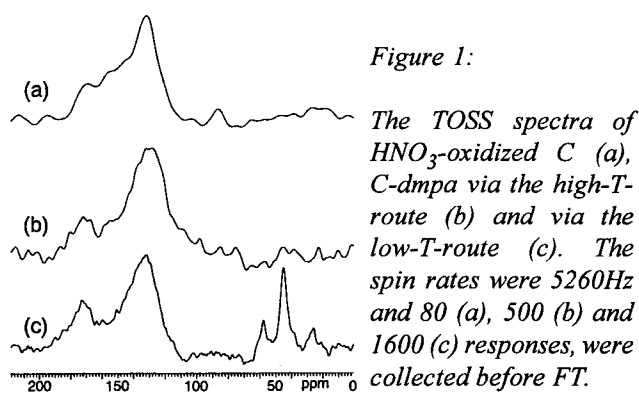
Two model compounds for dmpa-modified carbon were synthesized by methods analogous to those used for carbon modification. The model compounds were characterized by ¹³C NMR, ¹H NMR and IR spectroscopy.

The **low-T-model**, N-[3-(dimethylamino)propyl]benzamide, was prepared by drop-wise addition of 12g (86mmol) benzoyl chloride to 5.1g (55mmol) dmpa in 100ml 1.25M aqueous NaOH. The mixture was maintained below 5°C for one hour after which it was allowed to warm to room temperature. The product was extracted with diethyl ether and distilled[6].

The **high-T-model**, 2'-[3-(dimethylamino)propyl]carbamoil]-2-biphenylcarboxylic acid (mp 115-120°C, was synthesized by mixing 5g (22mmol) diphenic acid and 15g (150mmol) dmpa and heating the mixture at 200°C for 2hours, yielding 6g (22mmol) white product[7].

The 100.570MHz ¹³C MAS NMR spectra of the carbons were measured at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5mm Solids MAS Probe. Cross polarization with total side band suppression (TOSS) resulted in good spectra. Several thousand responses were collected before FT with 88Hz line broadening for TOSS on dmpa modified and oxidized C. The samples were washed with 1M NaOH and demineralized water and consecutively dried at 80°C/0.4mm Hg before measurement.

Results and discussion



The formation of the **high-T-model** compound, an asymmetric Zwitter-ion, indicates that attachment of dmpa to carbons is feasible via the **high-T-route**. Accordingly, in the ^{13}C NMR ($\text{CD}_3\text{OD} + \text{NaOD}$) spectrum 12 aromatic signals at δ -values 128 - 131 ppm and two C=O signals at δ -values 173 and 178 ppm are found. Furthermore, 4 alkyl signals are found at δ -values 27, 39, 45 and 58 ppm. The infrared C=O absorbance at 1712cm^{-1} is a prominent feature. ^1H NMR ($\text{DMSO } d_6$) spectrum: $\delta=1.0$ (2H, multiplet), $\delta=2.0$ (6H, singlet), $\delta=2.1$ (2H, triplet), $\delta=2.5$ (2H, triplet), $\delta=6.4-7.1$ (8H, multiplet).

The formation of the **low-T-model** compound shows that the **low-T-route** may as well be successful. ^{13}C NMR (CD_3OD) δ -values: 28.1, 39.3, 45.4, 58.3, 128.1, 129.5, 132.5, 135.7 and 169.9 ppm. ^1H NMR (CD_3OD): $\delta=1.8$ (2H, quintet), $\delta=2.2$ (6H, singlet), $\delta=2.4$ (2H, triplet), $\delta=3.4$ (2H, triplet) and $\delta=7.4-7.8$ (5H, multiplet).

^{13}C NMR TOSS experiments for modified C are shown in Fig. 1. The spectrum of C-dmpa prepared via the **low-T-route** yields the most information. Probably this modification leads to more uniform functional groups than the **high-T-route**, (for example because the **low-T-route** leads only to attachment via an amide instead of via amides and imides). The differences for other characterizations of the two routes are otherwise small. The TOSS spectrum of **low-T-route** C-dmpa is very similar to the ^{13}C NMR spectra of both the **low-** and **high-T-model** compounds. The aliphatic parts of these spectra are presented in Fig. 2 with the assignments. Therefore, the attached functional group is a N-[3-(dimethylamino)-propyl]carbonamide.

The N1s binding energy (BE) for XPS spectrometry of dmpa and dmea modified carbon R are at 399.9 and 399.7 eV, respectively. A t-amine group attached with an alkyl spacer (dmea) thus has almost the same binding energy as such a group together with an amide (or imide) group. Thus, the assignments of BEs to amides (399.9 eV) and lactams&imides (399.7 eV), determined by an XPS-

study of aminated and ammoxidated carbons, are confirmed.

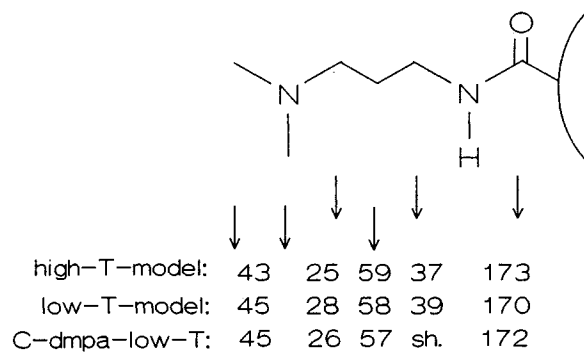


Figure 2: The structure of the surface functional group present on C-dmpa and the assigned ^{13}C NMR δ -values compared to those of the model compounds.

Conclusions

Unique ^{13}C NMR characterizations combined with an XPS-study revealed that chemical attachment of organic amines to the surface of activated carbons, via carboxylic acid chloride groups, results in one type of nitrogen functionality. Comparison of ^{13}C NMR spectra of 3-dimethylamino-propylamine modified carbons and model compounds shows that the tertiary amine group is attached via an N-alkyl amide or imide group. The overlap in binding energy of this amide or imide group with the binding energy of the nitrogen functional groups of aminated and ammoxidated carbons treated below 350°C affirms the assumed amide, lactam or imide groups for these carbons.

References

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