High-Resolution ^{13}C Solid-State NMR Study of Phenols Adsorption in Titania Nanotubes

Q. Chen (UNC-Chapel Hill, Physics and Astronomy); Zhehong Gan (NHMFL); Y. Wu (UNC-Chapel Hill, Physics and Astronomy)

Introduction

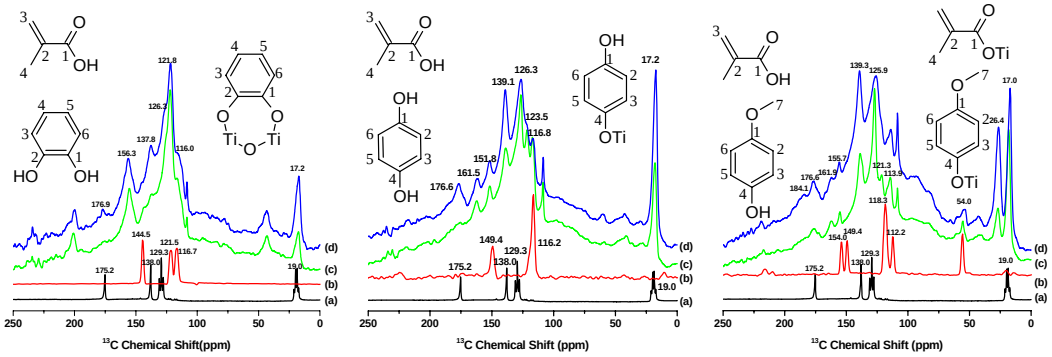
Phenolic adsorption on titanium dioxide surfaces is of great interest as they are crucial for understanding the strong adhesion of mussels on rocks, solar harvest efficiency of dye-sensitive solar cell, and surface reconstruction itself. We report here a ^{13}C solid state NMR study of the interaction of phenols with a titanium dioxide surface. This NMR study is challenging due to the disorder from defects and reconstruction and the low content of the adsorbed natural abundant molecules and requires the sensitivity and resolution of high magnetic fields.

Experimental

^{13}C spectra of different phenol adsorbed samples were collected on a 600 MHz spectrometer at the NHMFL using a 4mm Bruker MAS probe at 10kHz spinning rate.

Results and Discussion

Figure 1 compares the ^{13}C NMR spectra of catechol (left), hydroquinoe (center), and methoxylpheonol (right) on acid-washed (d) and water-washed (c) Titania nanotubes with the corresponding free molecule. The solvent used was methyl acrylic acid. The comparison reveals large changes in chemical shift from free molecules for the carbons forming Ti-O-C linkage, e. g. more than 11.8 ppm for C-1 and C-2 in catechol. The monodentate linkage to the surface results in a 12.1 ppm shift to C-4 in hydroquinone while only 2.4 ppm for carbon 1. The observed change is 12.5 ppm for C-4 of methoxylpheonol.



Conclusions

With improved resolution and sensitivity by high field, we have measured the change of chemical shift of phenols molecules induced by interactions with a titanium dioxide surface. The obtained information of chemical shift provides a direct probe of molecules on surface environment.

Acknowledgements

This project was supported by NSF, Grant No. DMR 0513915 and ARO, Grant No. DAAD19-03-1-0326.

References

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