



Low Temperature MAS NMR of Carbon Capture Materials

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Introduction

Solid amine sorbents are promising candidates to capture CO₂ from high concentration sources, such as flue gases. However, the mechanism of chemisorption by amines (on a solid support, such as SBA15 silica) is still not fully understood. Carbamate, carbamic acid, and bicarbonate are the products of the reaction of primary and secondary amines and CO₂. The formation of bicarbonate (facilitated by water) on solid amine sorbents has been debated in the past. In this project, a tertiary amine (dimethylaminopropylsilane, DMAPS) was used as a capture agent because it can only form bicarbonate. In an unexpected result, bicarbonate was found to separate into two distinct resonances upon cooling (in work published last year, Ref. 1). Notably, at room temperature, a single ¹³C resonance is found by “solid-state NMR”, but only using a Bloch decay sequence, suggesting motional averaging of the ¹³C-¹H dipole-dipole interaction when warm. The aim of this study is to better understand what leads to multiple bicarbonate environments.

Experimental

Dimethylaminopropylsilane (DMAPS) on SBA15 mesoporous silica was activated (at WU) under conditions of 105°C and 40 mtorr for 4 h. 40 mg of powder was mixed with 40 mg of DI water then packed into a glass tubing. The glass tubing was put into a sample holder then connecting to a gas manifold for ¹³CO₂ loading. The whole attachment was sealed and then shipped to NHMFL. Low temperature NMR experiments were conducted at NHMFL at 14.1 T with the Bruker 3.2 mm HCN LTMAS probe operating at a ¹³C resonance frequency of 150.89 MHz and ¹H of 600.11 MHz. The temperature was set to 100 K, and the spinning frequency was set to 10 kHz.

Results and Discussion

Figure 1 shows ¹³C{¹H} CPMAS of ¹³CO₂-reacted DMAPS at 100 K, and two bicarbonate signals are found. (Warming to room temperature shows a single ¹³C resonance, only, and most effective recorded by Bloch decay). The two signals at 162 ppm and 168 ppm are still in the process of being assigned. Figure 2 shows the ¹³C-¹H HETCOR spectrum at 100 K with a contact time of 150 μs. The 162 ppm resonance couples to two different types of protons, whereas the 168 ppm resonance appears to couple to a single type of proton. The 5.5 ppm value of the ¹H chemical shift is consistent with that of water, and our current efforts are focused on manipulating the chemical environment to help elucidate the details of the two bicarbonate sites.

Conclusions

It is shown that bicarbonate is formed in tertiary solid amine sorbents under conditions with water present. The low-temperature NMR afforded by NHMFL measurements enabled us to demonstrate that bicarbonate is likely undergoing motional averaging at room temperature, while at low temperature it surprisingly settles into two different, magnetically-inequivalent environments. These two environments are still under study. CPMAS is feasible at such low temperatures, which gives us confidence that the failure of CPMAS at higher temperatures is from dynamic averaging.

Acknowledgements

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References

[1] Chen, C.-H., *et al.*, *J. Am. Chem. Soc.*, **140**, 8648 (2018).

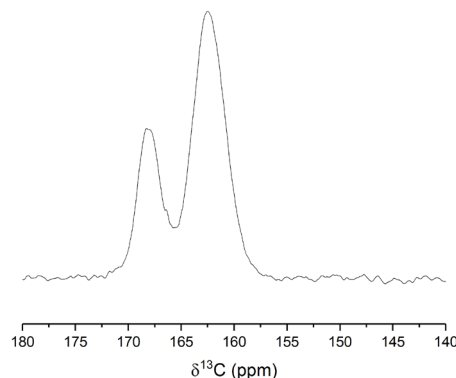


Figure 1. ¹³C{¹H} CPMAS of ¹³CO₂ loaded wet DMAPS at 100 K.

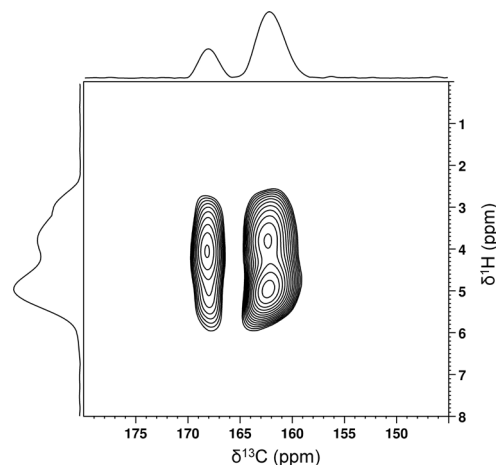


Figure 2. ¹³C-¹H HETCOR of ¹³CO₂ loaded wet DMAPS at 100 K.