



## Possible Misinterpretation in Surface Adsorption Studies by CP-MAS NMR

Oc Hee Han\* and Yoon Kyung Bae<sup>†</sup>

*Analysis Research Division, Daegu Center, Korea Basic Science Institute  
Daegu, 702-701, Republic of Korea  
Received April 17, 2008*

**Abstract** : Cross-polarization (CP) signals were observed even from liquid samples such as neat toluene. Therefore, CP signals of liquid molecules in the presence of high surface materials do not necessarily mean the molecules are adsorbed on solid surface, especially when no signal from the tertiary observing nuclei such as carbons of the molecules is detected.

**Keywords** : Cross-polarization, CP, CP-MAS, Adsorption, Adsorbate

### INTRODUCTION

One of the advantages of solid-state nuclear magnetic resonance (NMR) spectroscopy is that it can take the sample as it is: powder, single crystal, film, gel, lipid, bio-tissue, and even a mixture of powder and liquid or gas. It is especially important, to probe the samples as they are, for studying the chemical reactions and adsorption process on the interfaces. Consequently, in characterizing nano-materials with high surface area, this strong point of solid-state NMR plays a key role. Even before employing various advanced NMR methods such as heteronuclear correlation spectroscopic techniques,<sup>1-3</sup> molecular adsorption has been studied by relatively simple cross polarization-magic angle spinning (CP-MAS) NMR techniques.<sup>4,5</sup> CP-MAS techniques have been widely used to study molecular structure and dynamics of solid state bulk samples due to their improved sensitivity and spectral

\* To whom correspondence should be addressed. E-mail : ohhan@kbsi.re.kr

resolution by CP and MAS, respectively.<sup>1-3</sup> Presence of signals in the spectrum obtained by CP was interpreted as from the species, even in mobile state, with residual dipole interaction at least big enough to produce CP signals because CP process was known to occur through the dipole interaction between abundant and more polarized nuclear spin (I) and sparse and less polarized nuclear spin (S) (i.e.,  $^1\text{H}$  and  $^{13}\text{C}$ , respectively).<sup>1-3</sup> Therefore, molecular adsorption, especially organic molecules on coals<sup>4</sup> and acidic sites on solid acids,<sup>5</sup> have been one of the subjects intensively studied by CP experiments. In these high surface powder samples, some molecules are adsorbed more strongly than others because the adsorption takes place generally by attractive interaction between the surface and adsorbates such as acid-base,  $\pi - \pi$ , hydrophobic interaction and the attractive strength is different from one set of adsorbate and the surface to another.<sup>4,5</sup>

In this work, we demonstrated that the CP signal of liquid molecules from the mixture of solid and liquid samples would not necessarily mean that the species were adsorbed on solid surfaces since the CP signals were observed even from neat liquid samples.

## EXPERIMENTAL

### *Materials*

As reported previously,<sup>6,7</sup> SBA-15 was synthesized with Pluronic P123 [poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol); Mn ~ 5800; Aldrich, U.S.A.] triblock copolymer as a structure directing agent and tetraethyl orthosilicate (Aldrich, U.S.A.) as a silica source. In a typical synthesis, 4 g (0.69 mmol) of P123 was dissolved in 30 g of water and 120 g of 2 M HCl solution and then stirred at 35°C for an hour. Then, 8.5 g (40.8 mmol) of TEOS was added dropwise into the homogeneous solution while stirring at 35°C for 20 h. The obtained gel was aged at 100°C without stirring for 24 h. The solid white product, which was denoted as SBA-15-as-syn, was filtered, washed with distilled water and air-dried at room temperature. SBA-15-as-syn samples wetted with toluene were prepared by soaking SBA-15-as-syn in toluene for ~ 30 minutes and removing liquid toluene with Kimwipes just before NMR experiments. Anhydrous toluene (Aldrich, U.S.A.) as received was used without any purification process.

### *NMR Spectroscopy*

All solid-state NMR spectra were acquired on a DSX-400 spectrometer (Bruker Biospin GmbH, Germany) with a magnetic field strength of 9.4 T and 4 mm rotors at room temperature.  $^{13}\text{C}$  CP-MAS spectra were acquired with a 3 s pulse sequence repetition delay, a 5  $\mu\text{s}$  proton pulse length ( $90^\circ$  flip), a 2 ms contact time, a spectral width of 100 kHz, and a spinning rate of 0 ~ 4.5 kHz.  $^{13}\text{C}$  Single Pulse (SP)-MAS spectra under dipolar proton decoupling were obtained with a 3 s pulse sequence repetition delay and a 2  $\mu\text{s}$  carbon pulse length ( $36^\circ$  flip). All chemical shifts in ppm were referenced to external tetramethylsilane.

## RESULTS AND DISCUSSION

During our study on the influence of solvent on the dynamics of P123 surfactant remaining in SBA-15, small signals from toluene were detected in  $^{13}\text{C}$  CP-MAS spectra as shown for the methyl peaks of toluene in the bottom spectrum in Figure 1. The methyl signal was much larger in the  $^{13}\text{C}$  SP-MAS spectrum (top spectrum in Fig. 1). Thus it seems quite plausible to interpret that small amount of toluene was adsorbed on the surface of SBA-15 or occluded to P123 surfactants in SBA-15-as-syn. However, CP signals were observed even from neat toluene (bottom spectrum in Fig. 2). The smaller signals in the CP spectrum than the ones obtained with a single pulse sequence under strong proton decoupling (Fig. 2) can easily mislead to conclude that only a small portion of the liquid molecules is adsorbed on solid surface if the spectra were taken from the mixture sample of liquid and the high surface powder.

In addition, contact time variation experiments of liquid toluene produced the initial growth of the CP signal and then the signal decay after the maximum point as typically observed in the CP signal behavior of solid samples. A representative difference of the CP signal from solid-state and liquid-state molecules was that the signals only from protonated carbons were observed in the liquid samples as shown in Figure 2. Thus the  $^{15}\text{N}$  CP signal of unprotonated nitrogens of pyridine suggests that the pyridines were indeed adsorbed on the solid surface.<sup>5</sup> Another difference was that the CP matching powder range for liquid samples was much narrower than typical CP experiments on solid samples (not shown). The

mechanism explanation and application area of these CP phenomena of liquid samples will be published elsewhere.

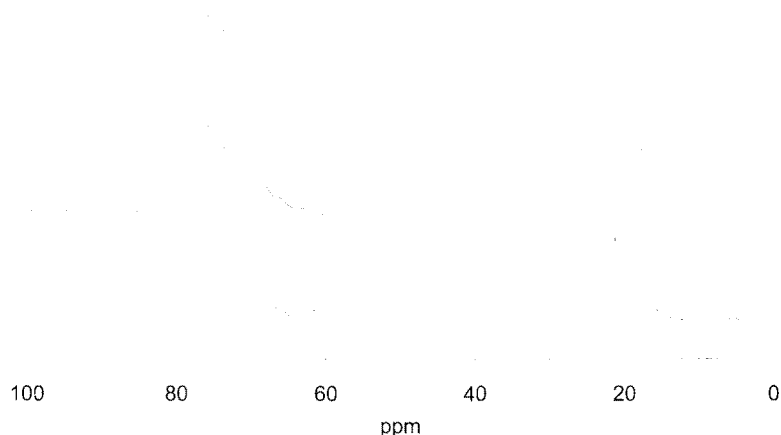


Fig. 1.  $^{13}\text{C}$  SP-MAS spectrum (top) and  $^{13}\text{C}$  CP-MAS spectrum (bottom) of SBA-15-as-syn wetted with toluene at 4.5 kHz spinning rate. The methyl peaks of toluene appear near 22 ppm and all the other peaks are of P123 as assigned in reference 7.

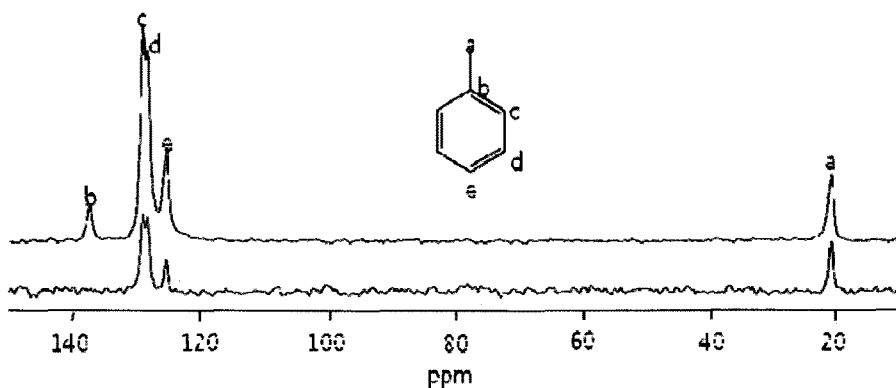


Fig. 2.  $^{13}\text{C}$  SP static spectrum (top) and  $^{13}\text{C}$  CP static spectrum (bottom) of neat toluene only. The number of acquisition was 32 and 337 for SP and CP spectrum, respectively.

In summary, we report that CP signals of liquid molecules in the presence of high surface materials do not necessarily mean the molecules are adsorbed on solid surface, especially when no signal was observed from the tertiary carbons of the molecules. To avoid

this kind of misinterpretation possibility, simple CP experiments on the same liquid sample only are suggested. Precaution is required for the CP experiments since there is a possibility that the CP matching condition is not exactly the same for the mixture samples and the liquid only samples.

### ***Acknowledgement***

This work was supported initially by the Korea Research Foundation Grant, KRF-2003-015-C00410 and partly by the Korea Research Council of Fundamental Science & Technology (STRM grant PG7069). Ms. Sun Ha Kim at Daegu Center, KBSI was acknowledged for preparing Figure 2.

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