

CHROM. 13,335

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### Characterization of silica-attached systems by $^{29}\text{Si}$ and $^{13}\text{C}$ cross-polarization and magic-angle spinning nuclear magnetic resonance

GARY E. MACIEL\*, DEAN W. SINDORF and VICTOR J. BARTUSKA

*Department of Chemistry, Colorado State University, Fort Collins, CO 80523 (U.S.A.)*

(Received August 15th, 1980)

During recent years, there has been a great deal of activity in the synthesis, characterization and application of materials prepared by attaching organic or organo-metallic moieties to silica or silica gel surfaces<sup>1-6</sup>. These kinds of materials are of interest because they permit the transfer of some properties encountered in homogeneous chemistry to an immobilized (or less mobilized) state. This kind of situation finds great utility for stationary phases in separation science<sup>1-4</sup> and in catalysis<sup>5,6</sup>.

Among the more promising types of materials developed in recent years for chromatography are the silica-attached organics<sup>1-4</sup>. Although standard pulsed Fourier-transform nuclear magnetic resonance (NMR) techniques can be used to study analogues of these materials in liquid solution, the solid materials themselves are not amenable to such techniques because the low level of mobility in these systems, at least near the silica surface, causes a great deal of line broadening due to magnetic dipole-dipole interactions with protons and chemical-shift anisotropy<sup>7,8</sup>. However, the recently developed techniques of cross polarization and magic-angle spinning (CP-MAS)<sup>7-9</sup> permit one to obtain NMR spectra on solids with a quality approaching that obtained routinely on liquids. We have undertaken an intensive CP-MAS study of materials prepared by attaching organic moieties to silica surfaces, using both  $^{29}\text{Si}$  and  $^{13}\text{C}$ . Chang *et al.*<sup>10</sup> have reported a  $^{13}\text{C}$  cross-polarization study, without magic-angle spinning, on some organic derivatives of chrysotile asbestos. The present note is a preliminary report of  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS studies of stationary phases based on organic derivatives of silica gel.

## EXPERIMENTAL

Materials employed in this study were prepared by standard techniques or acquired from other laboratories, as indicated in the figure captions. The CP-MAS measurements were made on a modified JEOL FX-600 spectrometer operating at 11.88 MHz.

## RESULTS AND DISCUSSIONS

The  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS NMR spectra of four representative systems are shown in Figs. 1 to 4. The chemical-shift conventions are in ppm with respect to the

$^{29}\text{Si}$  or  $^{13}\text{C}$  resonance of liquid tetramethylsilane; higher numbers correspond to lower shielding. Considering bulk susceptibility effects, for which corrections have not been made, the sample-to-sample shifts should be considered accurate to within *ca.*  $\pm 1$  ppm. Internal shifts within a spectrum are accurate to within *ca.*  $\pm 0.1$  ppm. Peak intensities depend on  $^{29}\text{Si}$ - $^1\text{H}$  and  $^{13}\text{C}$ - $^1\text{H}$  cross-polarization dynamics, and should not be used quantitatively until detailed studies of these factors have been carried out. As the  $^{29}\text{Si}$ - $^1\text{H}$  cross-polarization efficiency decreases as the Si-H distance increases, internal Si atoms of the silica framework should not contribute to the CP-MAS spectra.

Fig. 1 shows spectra of a sample prepared by the reaction of  $(\text{CH}_3)_3\text{SiCl}$  with silica gel (SG2, made according to the procedure of Peri and Hensley<sup>11</sup>)<sup>12</sup>. The  $^{13}\text{C}$  spectrum (Fig. 1A) shows a single resonance at 2.2 ppm, corresponding to the attached  $-\text{Si}(\text{CH}_3)_3$  group in a silica-attached species of the type  $\equiv\text{SiO}-\text{Si}(\text{CH}_3)_3$ , (I). The  $^{29}\text{Si}$  spectrum (Fig. 1B) is more complex, showing definite peaks at  $-107.2$ ,  $-99.3$  and  $15.4$  ppm. Based on previous reports of  $^{29}\text{Si}$  studies on aqueous silicate systems<sup>13,14</sup>, and on our work on  $^{29}\text{Si}$  cross-polarization relaxation times<sup>15</sup>, we can assign the  $^{29}\text{Si}$  peak at *ca.*  $-107$  ppm to Si atoms at the surface of the silica gel, each

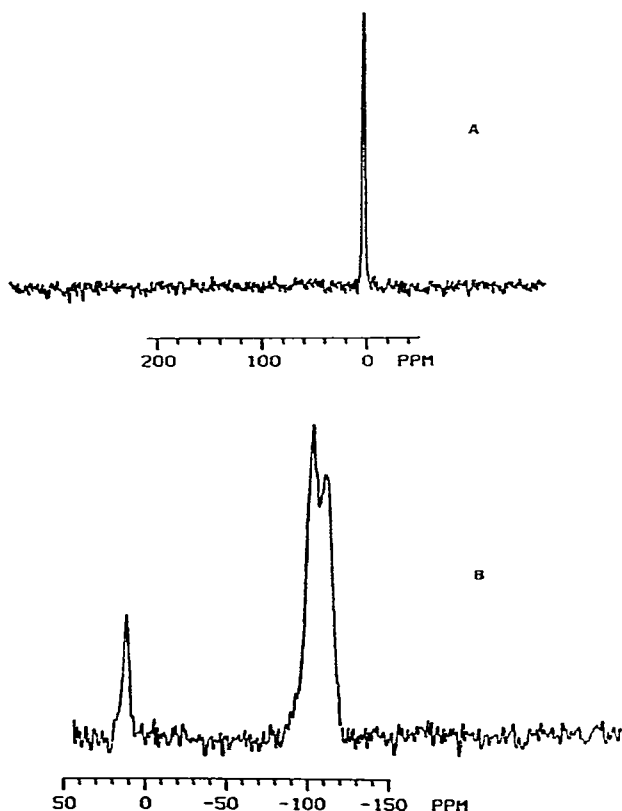


Fig. 1. CP-MAS spectra of the reaction product of  $(\text{CH}_3)_3\text{SiCl}$  with silica gel: A,  $^{13}\text{C}$  spectrum; B,  $^{29}\text{Si}$  spectrum.

bonded to four  $-\text{O}-\text{Si}\equiv$  moieties, and the  $^{29}\text{Si}$  peak at *ca.*  $-99$  ppm to surface Si atoms bound to one  $-\text{OH}$  group and three  $-\text{O}-\text{Si}\equiv$  moieties. The  $^{29}\text{Si}$  peak at  $15.4$  ppm is assigned to the  $-\text{O}-\text{Si}(\text{CH}_3)_3$  group introduced by the silylating reagent.

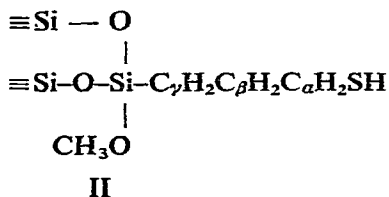


Fig. 2. shows spectra of a sample provided by Pirkle and his co-workers and prepared from the silylating agent  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$ . The  $^{13}\text{C}$  spectrum (Fig. 2A) shows a resonance at  $50.2$  ppm that can be assigned to the methyl C atom in a silica-attached structure of type II, a peak at  $27.9$  ppm that can be assigned to the  $\alpha$  and  $\beta$  methylene C atoms in II and a peak at  $11.3$  ppm that can be assigned to the methylene C atom adjacent to Si in II. The  $^{29}\text{Si}$  spectrum (Fig. 2B) shows peaks at  $-107.9$  and  $-99.8$  ppm that are identifiable with the silica-gel surface, as described for Fig. 1 (with a hint of a shoulder at *ca.*  $-89$  ppm to be associated with surface Si

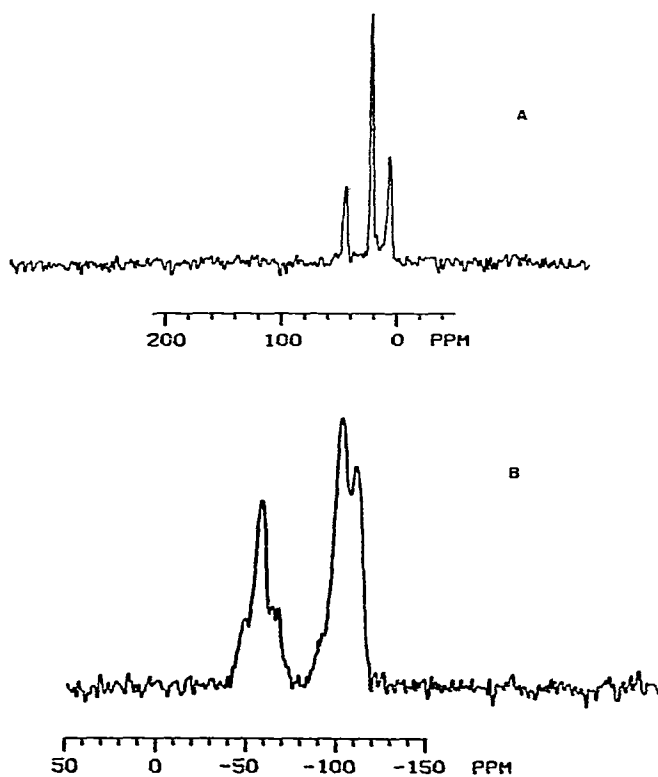


Fig. 2. CP-MAS spectra of the reaction product of  $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$  with silica gel (sample provided by W. Pirkle): A,  $^{13}\text{C}$  spectrum; B,  $^{29}\text{Si}$  spectrum.

atoms attached to two  $-\text{O}-\text{Si}\equiv$  moieties and two  $-\text{OH}$  groups), and peaks to be identified with the attached silylating group. The strong peak at  $-56.6$  ppm is identified with the Si atom shown for structure II; the shoulder at  $-48.8$  ppm can be identified with Si atoms of species in which one of the  $\equiv\text{Si}-\text{O}-$  groups shown in II is replaced by a second  $\text{CH}_3\text{O}-$  group; the shoulder(s) at *ca.*  $-65$  ppm can be identified with species in which the  $\text{CH}_3\text{O}-$  group of II is replaced by a third  $\equiv\text{Si}-\text{O}-$  group.

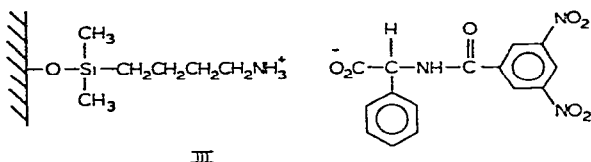


Fig. 3 shows spectra of another sample provided by Pirkle and co-workers, with the presumed structure III. The  $^{13}\text{C}$  spectrum is highly complex, with peaks in both the aromatic-C and aliphatic-C regions, and can be interpreted in terms compatible with a stationary phase with a structure of the general type III. The  $^{29}\text{Si}$  spectrum shows peaks at  $-108.5$  and  $-100.0$  ppm, corresponding to Si atoms at

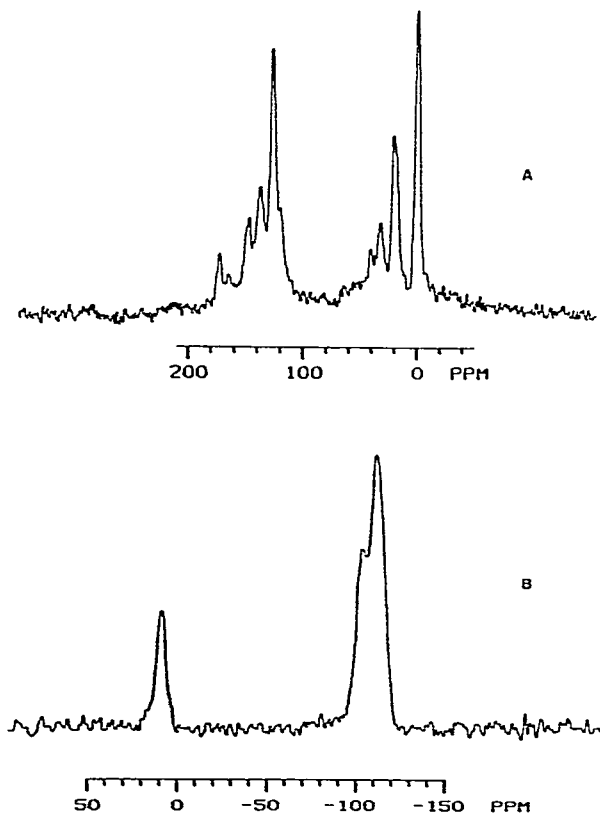


Fig. 3. CP-MAS spectra of the Pirkle's stationary phase (III): A,  $^{13}\text{C}$  spectrum; B,  $^{29}\text{Si}$  spectrum.

the surface of the silica gel, and a peak at 12.7 ppm, corresponding to the Si atom shown in structure III.

Fig. 4 shows the  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS spectra of the commercially available stationary phase Spherisorb  $\text{C}_{18}$ ,  $10\ \mu\text{m}$  (Phase Separations, Queensferry, Great Britain). The  $^{13}\text{C}$  spectrum of this sample (Fig. 4A) shows a dominant peak at 31.0 ppm, which can be identified with the internal methylene C atoms of a long hydrocarbon chain. The smaller peaks at 13.7, 23.5 and 1.7 ppm are compatible with resonance positions for terminal methyl C atoms, for methylene C atoms adjacent to the terminal methyl groups and for C atoms attached to Si atoms, respectively. The  $^{29}\text{Si}$  spectrum of Spherisorb (Fig. 4B) has the dominant silica gel peaks at  $-108.5$  and  $-97.6$  ppm, and smaller resonance peaks at  $-64.9$ ,  $-54.7$  and  $16.0$  ppm. These last three peaks can be identified with Si atoms at the silica surface with local environ-

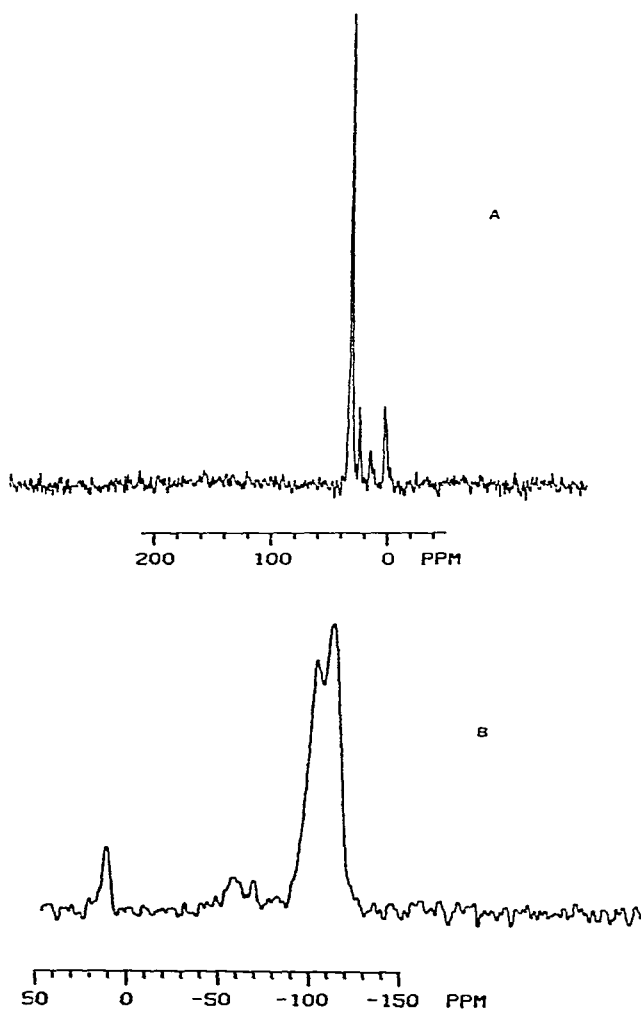


Fig. 4. CP-MAS spectra of Spherisorb: A,  $^{13}\text{C}$  spectrum; B,  $^{29}\text{Si}$  spectrum.

ments in which there are three  $\equiv\text{Si-O}$  groups and a C atom (alkyl group) attached; two  $\equiv\text{Si-O}$  groups, a hydroxyl group and a C atom (alkyl group); and one  $\equiv\text{Si-O}$  group with three alkyl groups attached.

In order to gain additional information on the structures and local mobilities of the kinds of systems described here, or to elucidate the quantitative meanings of the intensities, one must consider the details of spin dynamics in the CP-MAS experiment; such work is in progress. Nevertheless, as demonstrated here, even without detailed spin-relaxation studies, one can readily obtain valuable structural information on stationary chromatographic phases based on silica gel from a combination of  $^{29}\text{Si}$  and  $^{13}\text{C}$  CP-MAS studies.

#### ACKNOWLEDGEMENTS

The authors are grateful to Professor William Pirkle of the University of Illinois for providing some of the samples, to Dr. I. Ssuer Chuang, who performed some preliminary experiments on these samples and to the National Science Foundation for providing partial support of this work under Grant No. CHE 74-23980. The authors also gratefully acknowledge use of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. 78-18581, in obtaining  $^{29}\text{Si}$  spectra of related liquid samples.

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