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CHARACTERIZATION OF γ-AMINOPROPYL AND N-β(AMINOETHYL)γ-AMINOPROPYL GROUPS IMMOBILIZED ON SILICA GEL BY USING CMR SPECTROSCOPY

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The organofunctional groups immobilized on silica gel, $NH_2CH_2CH_2CH_2Si$-(silica) and $NH_2CH_2CH_2NHCH_2CH_2CH_2Si$-(silica), have been characterized by CMR spectroscopy in the suspended state. The carbon adjacent to silicon showed substantial low-field shift and T_1 reduction as a result of immobilization. The microenvironment of these amino and diamino groups resembles that in the homogeneous phase in appropriate solvents, owing to the permissible segmental motion of the three-carbon chain.

Organofunctional groups, bonded to solid surfaces, are indispensable to the immobilization of soluble complex catalysts1) or to the column packing materials for affinity chromatography.2) Proper methods to characterize them have long been looked for. CMR spectroscopy was once applied to the modified silica gels, but their spectral resolution was rather poor.3) We have found that satisfactory measurement is possible for $NH_2CH_2CH_2CH_2Si$-(silica) (N-ligand-(silica)) and $NH_2CH_2CH_2NHCH_2CH_2CH_2$-Si-(silica) (N,N-ligand-(silica)), when appropriate solvents are used as the suspending medium. CMR information based on both the chemical shift and the spin-lattice relaxation time (T_1) is very important in order to characterize the chemical entity and the motional situation of organic moieties on the surface.

Binding procedure and spectral measurement. To the toluene (100 ml) solution of silane ($NH_2CH_2CH_2CH_2Si(OEt)_3$, Shin-Etsu Chem. Ind. Ltd.; 15.6 g), water (3.08 g) and then silica gel (10 g) was added with stirring, and the mixture was refluxed for 24 h. Silica gel was evacuated at 200°C (4 h) before use. The amount of water was equivalent to that necessary for hydrolyzing alkoxy groups of silane. After cooling, the sample was transferred to a Soxhlet apparatus, extracted with benzene for 24 h, and dried in vacuo (130°C, 4 h). Binding procedure for $NH_2CH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$ (Shin-Etsu Chem. Ind. Ltd.) was performed similarly with the following amounts of reagents used: silane 20.8 g, toluene 100 ml, water 5.10 g, and silica gel 15 g. The BET surface area was markedly reduced from 169.3 m^2/g to 10.3 m^2/g for N-ligand-(silica) and to 13.1 m^2/g for N,N-ligand-(silica) by the overall treatment. The amounts of immobilized ligand were 3.9 meq/g for the former and 2.7 meq/g for the latter as determined from the elemental analysis.

Spectra were obtained with noise-modulated proton decoupling on a Fourier transform pulsed NMR spectrometer (JEOL FX-60), operating at 15.04 MHz. Field-frequency control (lock) was effected by means of a solvent deuterium resonance. The chemical shifts were measured relative to the external 1,4-dioxane reference and are reported

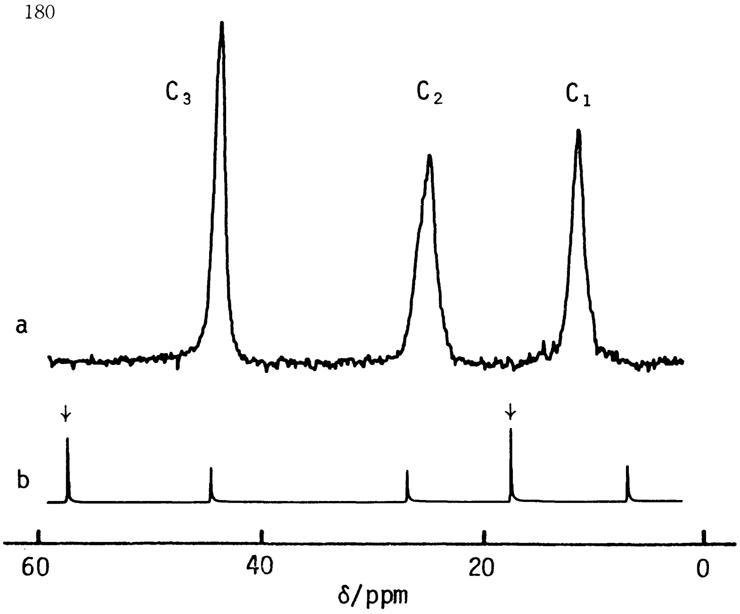

Fig. 1. CMR spectra of the organofunctional groups immobilized on silica and of original alkoxysilane (15 MHz, 22000 scans).
(a) $NH_2CH_2CH_2CH_2Si$-(silica) in D_2O suspension.
(b) $NH_2CH_2CH_2CH_2Si(OCH_2CH_3)_3$ in neat liquid.
Numbers are designated from the silicon atom. Arrows indicate the ethoxy carbon resonances. 10 μsec pulse width, 2.0 sec pulse interval.

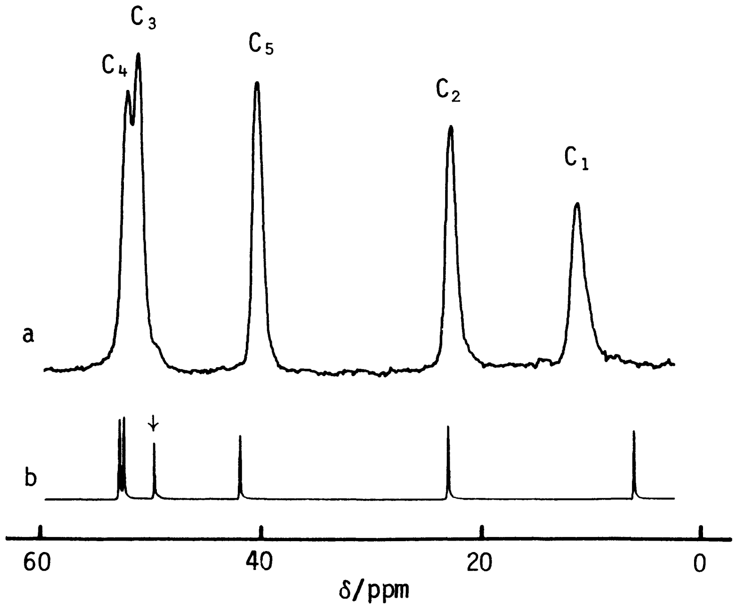

Fig. 2. CMR spectra of the organofunctional groups immobilized on silica and of original alkoxysilane (15 MHz, 25000 scans).
(a) $NH_2CH_2CH_2NHCH_2CH_2CH_2Si$-(silica) in D_2O suspension.
(b) $NH_2CH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$ in neat liquid.
Numbers are designated from the silicon atom. An arrow indicates the methoxy carbon resonance. 10 μsec pulse width, 2.0 sec pulse interval.

in ppm downfield from TMS using the conversion: δ(TMS) = δ(dioxane) - 67.4 ppm. Before the measurement, the suspended sample (0.5 g) in the deuterio-solvent (1.5 ml) was sedimented in an NMR sample tube (10 mmϕ) on standing overnight at room temperature. The gel particles were aggregated to form a packed layer at the bottom part of the tube, leaving a supernatant liquid (∿0.5 ml) above it. The layer was thick enough (∿1.5 cm) to cover the range of the NMR detection coil, and was fixed with a Teflon stopper. The amount of the solvent therein was sufficient to give the deuterium resonance for the field-frequency control. It is noteworthy that line widths were dependent on the solvent used; the order of the solvent to give better resolution was water > methanol > chloroform >> benzene. In benzene, all the peaks were very broad and were hardly detected.

<u>^{13}C Chemical shifts</u>. Figures 1 and 2 present the CMR spectra of N-ligand-(silica) and N,N-ligand-(silica) in D_2O, respectively. The absence of alkoxy groups in both spectra confirms that they were completely removed in the course of binding treatments. Line widths were in the range of 15-25 Hz. The peaks were assigned in accordance with the established values of chemical shift for aliphatic amine and diamine compounds.[4)] The chemical shift data are tabulated in Table 1. It is obvious that in both cases

C_1 carbon (designated from the silicon atom) was substantially shifted to lower field as a result of immobilization.

C_3 carbon and ethylene diamine carbons were virtually unaffect-

Table 1. ^{13}C Chemical Shifts of the Organofunctional Groups Immobilized on Silica and of Original Alkoxysilane[a]

sample		medium	chemical shift/ppm				
organofunctional group	state		C_1	C_2	C_3	C_4	C_5
$NH_2CH_2CH_2CH_2Si$-	silane	neat	7.3	27.2	44.8		
	silica	D_2O	11.5	24.8	43.7		
$NH_2CH_2CH_2NHCH_2CH_2CH_2Si$-	silane	neat	6.4	23.1	52.3	52.7	41.8
		$CDCl_3$	6.8	23.3	52.5	52.5	42.0
	silica	D_2O	11.7	23.0	51.0	52.0	40.4
		$CDCl_3$	10.7	23.4	52.3	52.3	41.4

[a] Numbers are designated from the silicon atom.

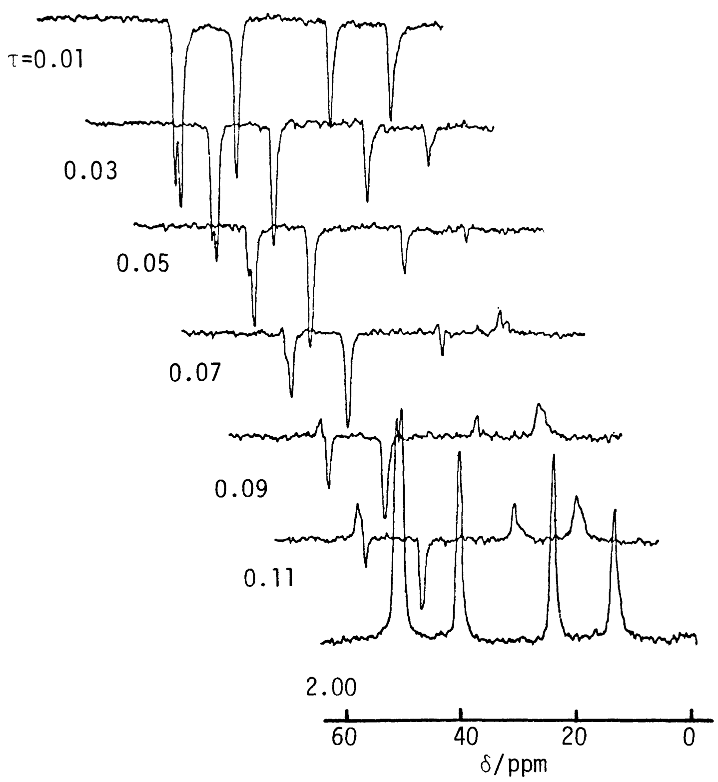

Fig. 3. Spin-lattice relaxation spectra of $NH_2CH_2CH_2NHCH_2CH_2CH_2Si$-(silica) suspended in D_2O (15 MHz, τ in sec, T: 2.0 sec).

ed. Solvent effect on chemical shift was rather small in comparison with the effect of immobilization. It is of interest that 2-butenes[5)] and toluene[6)] adsorbed on silica or Zeolite show low-field shift for the carbon atoms pertinent to adsorption. Common factors may determine the ^{13}C chemical shifts of the surface organic species.[7)]

Spin-lattice relaxation times.

T_1 was determined by the inversion-recovery method.[8)] Figure 3 clearly shows the order of recovery rate in the carbons of N,N-ligand-(silica). The values of T_1 are summarized in Table 2. All the carbon atoms reduced the T_1 values upon immobilization, and the degree of reduction was most pronounced for C_1 carbon. Two origins may be invoked for the observed enhancement of relaxation rates:[9)] (1) paramagnetic impurities in the silica gel, and (2) decrease in the freedom of motion due to the anchoring of the silicon atom. We consider that the former is improbable on the following reasons: (i) the values of ^{13}C-^{1}H nuclear Overhauser effect were determined as 1.3 (C_1) and 1.6 (C_2) for N,N-ligand-(silica) in $CDCl_3$, which are close to the maximum value of this effect (1.987) and indicate the predominance of ^{13}C-^{1}H dipole-dipole interactions in the relaxation of these carbon atoms,[8)] and (ii) the T_1 values of C_1 carbon are significantly different between N-ligand-(silica) and N,N-ligand-(silica).

The observed magnitude of T_1 is reasonable for the aliphatic chain whose trans-

Table 2. Spin-Lattice Relaxation Times of the Organofunctional Groups Immobilized on Silica and of Original Alkoxysilane[a]

sample		medium	T_1/sec				
organofunctional group	state		C_1	C_2	C_3	C_4	C_5
$NH_2CH_2CH_2CH_2Si-$	silane	neat	2.27	3.03	3.16		
	silica	D_2O	0.21	0.35	0.36		
$NH_2CH_2CH_2NHCH_2CH_2CH_2Si-$	silane	neat	0.98	0.98	0.97	1.28	1.49
		$CDCl_3$	1.82	1.82	2.13[b]	2.13[b]	2.16
	silica	D_2O	0.10	0.14	0.20	0.14	0.37
		$CDCl_3$	0.08	0.13	0.28[b]	0.28[b]	0.40

[a] Numbers are designated from the silicon atom. [b] Obtained from the coincident peaks.

lational motion is hindered but internal rotation is almost free, when compared with those measured for the n-butyl group anchored in poly(n-butyl methacrylate) (T_1 in sec: C_1 0.12, C_2 0.31, etc.).10) The increase of T_1 from C_1 to C_2 to C_3 reflects the ease of motion in that order. Taking into account also the fact that chemical shifts of C_3 carbon and ethylene diamine carbons are essentially invariant upon immobilization, the amino or diamino group may exist under a microenvironment similar to that in homogeneous solutions. The advantage of polar solvents in the measurement may lie in that they prevent the possible interaction of the amino group with the surface,11) which would restrict the segmental motion further to cause the failure of spectral resolution.

References.

1) F. R. Hartley and P. N. Vezey, "Advances in Organometallic Chemistry", Vol. 15, Academic Press, New York, N. Y. (1977), pp. 189-234.
2) K. Unger and D. Nymath, Chromatographia, 7, 63 (1974).
3) J. J. Chang, A. Pines, J. J. Fripiat, and H. A. Resing, Surface Sci., 47, 661 (1975).
4) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N. Y. (1972), p. 152.
5) I. D. Gay and J. F. Kriz, J. Phys. Chem., 82, 319 (1978).
6) D. Deininger, D. Geschke, and W.-D. Hoffmann, Z. Physik. Chem. (Leipzig), 225, 273 (1974).
7) D. Michel, Surface Sci., 42, 453 (1974).
8) J. R. Lyerla, Jr. and G. C. Levy, "Topics in Carbon-13 NMR Spectroscopy", Vol. 1, John Wiley & Sons, New York, N. Y. (1974), pp. 79-148.
9) I. D. Gay, J. Phys. Chem., 78, 38 (1974).
10) G. C. Levy, J. Amer. Chem. Soc., 95, 6117 (1973).
11) U. Edlund, C. Holloway, and G. C. Levy, ibid., 98, 5069 (1976).

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