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Characterization of Aluminophosphate Surfaces via ^{29}Si CP/MAS NMR

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The ^{29}Si CP/MAS spectra of the reaction products of hexamethyldisilazane (HMDS) with porous aluminophosphates showed distinct resonances from trimethylsiloxane groups attached to both aluminum and phosphorus. The relative intensity of the two signals varied according to the composition of the carrier; however, integration always indicated a higher phosphorus to aluminum ratio in the silane product than expected from the bulk composition. This can be explained by either a nonhomogeneous distribution of phosphorus and aluminum centers or a hindered reaction mechanism at the surface. In either case, the reaction products of HMDS with the aluminophosphate surface can be used to predict the behavior of other substrates at this surface, such as catalytically active chromium compounds. The spectra of the reaction products obtained with dichlorodimethylsilane suggest not only dimethylsiloxane groups bridging aluminum/phosphorus centers but also phosphorus/phosphorus and aluminum/aluminum bridges. © 1989 Academic Press, Inc.

I. INTRODUCTION

The chemical composition and reactivity at the surface of catalysts and catalyst carriers are areas of primary importance to our understanding the catalytic process. As a consequence, the application of analytical techniques to the investigation of surfaces has long remained an active field of study. One early catalyst surface to be studied was silica–alumina, whose catalytic activity was found to be primarily dependent on the acidity of the surface and the associated cations. Early work involved measurement of the acid strength of the surface and quantitation of the acidity of the surfaces via titration with amine bases (*1*).

More recently infrared spectroscopy has been used to investigate the surfaces of alumina, silica gel, silica–alumina, and aluminophosphates (*2–6*). Reactions of these surfaces with pyridine, ammonia, and carbon dioxide yield surfaces labeled with species that can be identified and measured directly. This "probe" molecule approach has several advantages, one being tailoring the probe molecule for a particular reaction. In the above studies the pyridine and ammonium probes were used to examine both types of acid sites, Brønsted and Lewis, while carbon dioxide was used to examine only the Brønsted sites. In this manner, models of these surfaces have been constructed leading to a better understanding of their catalytic properties.

With the introduction of NMR spectrometers capable of examining materials in the solid state, a resurgence in the characterization of catalytic surfaces has occurred. For the most part, the NMR studies also use the probe molecule approach. Alumina has been examined by ^{13}C cross-polarization/magic angle spinning (CP/MAS) using pyridines or alkyl amines as the probes (*7, 10*). The spectra obtained show signals from amines complexed with both Lewis and Brønsted acid sites.

The surface of alumina has also been examined using ^{15}N CP/MAS NMR (*11, 12*). Pyridine and butylamine have been used as probe molecules with the resulting ^{15}N spectra showing signals from physisorbed species as well as the Lewis and Brønsted acid sites. In addition, the resolution is sufficient to differentiate between different Lewis acid sites.

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An extension of this technique is the use of phosphorus bases as probes and ^{31}P CP/MAS as the spectroscopy tool. Lunsford and co-workers have examined zeolites using trimethylphosphine as the probe (*13, 14*). The spectra they obtained showed a wealth of data with discrimination not only between Brønsted and Lewis acid sites but also between different Lewis acid sites in the zeolites and a second Brønsted site which seemed associated with a Lewis site. Maciel and co-workers have extended this approach further to amorphous silica–alumina and have added another probe molecule class, phosphine oxides (*15–17*).

The surface of silica gel has been examined both with and without chemical probes. ^{29}Si CP/MAS NMR has been used to study the hydroxyl groups on the surface directly (*18–20*). In this manner three different types of silicon centers were detected, with two of these centers associated with the surface.

The most common chemical probe used for silica gel surfaces has been the trimethylsilane (TMS) group (*21–23*). The method using this molecular probe is slightly different than the method using the amine and phosphorus bases. The TMS group is reacted with the surface forming a covalent bond rather than the acid/base reaction characteristic of the amine and phosphine probes. This approach is especially well suited to the study of surface hydroxyl groups since the reaction products are stable to the atmosphere. However, one drawback is the absence of information on Lewis acid sites. Using the TMS probe, the presence of mono- and dihydroxyl surface silicon centers in silica gel has been unequivocally proven.

Interest in the structure of aluminophosphates stems from the recent advances in the preparation and use of these materials (*24–28*). With various phosphorus to aluminum (P/Al) ratios, the properties of aluminophosphates can change dramatically. This is clearly seen by the behavior of ethylene polymerization catalysis systems placed on the surface of aluminophosphates (*26, 28, 30, 31*). The presence of a bimodal distribution of molecular weights in polymers obtained from one such catalyst system is suggestive of the presence of two chemically distinct polymerization sites with the concentrations dependent on the P/Al ratio of the support.

The presence of both phosphorus and aluminum hydroxyl groups on the surface of $AlPO_4$ (P/Al = 1) has previously been confirmed using infrared (*4*). Two OH stretching bands were observed at 3680 and 3800 cm^{-1}, assigned to the phosphorus and aluminum hydroxyl groups, respectively. In addition to these two types of Brønsted acid sites, Lewis sites were also detected using carbon dioxide, ammonia, and pyridine as probe molecules. The absence of bands between 2360 and 2380 cm^{-1} upon addition of carbon dioxide suggested the Lewis acid sites were relatively weak.

This paper focuses on the application of ^{29}Si CP/MAS NMR to the detection and quantitation of the surface hydroxyl groups in aluminophosphates. Although both phosphorus hydroxyl groups and aluminum hydroxyl groups have been detected in $AlPO_4$, the presence of both types of groups has yet to be proven for aluminophosphates with a phosphorus to aluminum ratio less than one. In addition, although previous work indicated a homogeneous dispersion of phosphorus atoms within the aluminum atom matrix (*27*), the dispersion of the phosphorus hydroxyl groups at the surface is unknown. Thus, reaction of these carriers with silating agents should provide insight into the attachment of organochromium compounds (single attachment) and/or chromium oxides (double attachment).

II. EXPERIMENTAL

All of the carriers used in this study were highly porous materials suitable for use as polymerization catalyst (PV = 1.4–2.0 cc/g; A = 250–400 m^2/g). Aluminophosphates were prepared as previously described

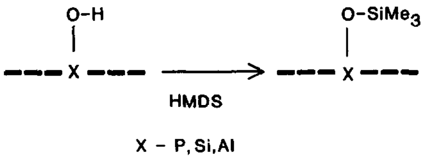


FIG. 1. Reaction of hexamethyldisilazane with surface hydroxyl groups.

(*27*, *30*). Ketjen B alumina and Davison 952M silica were also used. Before use, these carriers were usually calcined in dry air at 600°C for 3 h to remove traces of organics. In many experiments a near fully hydroxylated surface was desired. Thus, after being calcined these supports were soaked overnight in liquid distilled water and then dried under a dry nitrogen stream for 3 h at 200°C. Phosphated silica was prepared by impregnating 86 mmol of phosphoric acid onto 20 g of silica and drying at 200°C.

To silate these materials, about 10 g of the carrier was fluidized in a glass tube under dry nitrogen in a 5-cm-deep bed. A furnace around the tube maintained the temperature at 150°C. Two milliliters of the silating agent was then injected into the nitrogen stream for about 30 min. There it evaporated at 25°C and was carried up through the support bed. After all of the silating agent was gone the bed was flushed with nitrogen at 150°C for another 30 min to remove all traces of unreacted reagent. Samples were transferred, under nitrogen, to a glove bag and loaded into Doty-type cylindrical CP/MAS rotors and sealed with Kel-F endcaps. The samples were found to be stable over several days under these conditions, with no evidence of hydrolysis. Hexamethyldisilazane (HMDS) was purchased from Petrarch, dichlorodimethylsilane (DCDMS) from Aldrich, and trimethylethoxysilane and dimethyldiethoxysilane from Fluka.

The NMR spectra were obtained under CP/MAS conditions with a spinning speed of 4 kHz on an IBM WP-200-SY spectrometer operating at 37.75 MHz for ^{29}Si. A 5.1-μs (90°) pulse for the irradiation channel and a 6-ms contact time were used to transfer magnetization to the silicon nuclei. A pulse delay of 5 s and acquisition time of 0.13 s assured full relaxation between pulses. Tetrakis(trimethylsilyl)methane (−1.39 ppm) was used as an external reference. The magic angle was set by observing the resonances of octakis(trimethylsiloxy)-silsesquioxane.

III. RESULTS AND DISCUSSION

Singly Attached Species (TMS)

The reaction of HMDS with surface hydroxyl groups forms trimethylsiloxyl (TMS) groups at the surface with the ^{29}Si NMR chemical shift dependent on the type of surface. The basic reaction is shown in Fig. 1. Three "standards" were prepared to determine the representative chemical shifts of TMS groups bound to different types of surfaces. The spectra obtained for silica, phosphated silica, and alumina are shown in Fig. 2 and are representative of surface trimethylsiloxyl groups attached to silicon, phosphorous, and aluminum.

Not surprisingly, the spectrum of the reaction product with silica gel was essentially identical to that previously reported by Maciel and Sindorf using trimethylchlorosilane (*21*). The spectra showed the major resonance at 13 ppm, from the trimethylsiloxyl group attached to a surface silicon, and a minor resonance at 18 ppm.

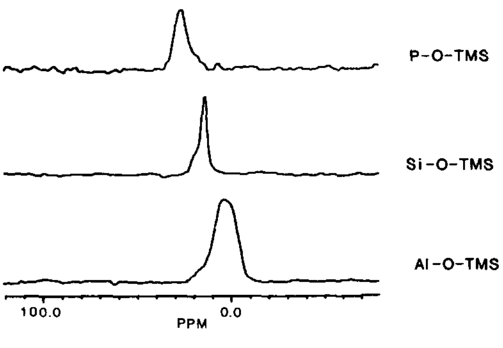


FIG. 2. ^{29}Si CP/MAS NMR spectra of trimethylsilyl groups bound to surface hydroxyl groups.

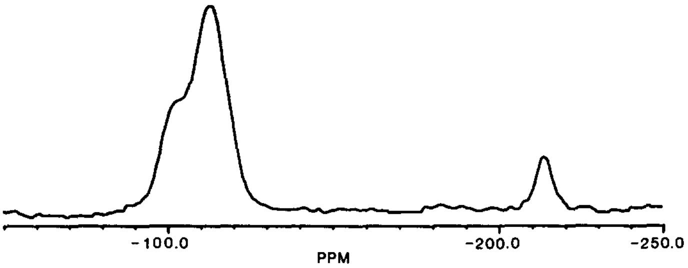


FIG. 3. ^{29}Si CP/MAS NMR spectrum of a phosphated silica gel.

This latter signal, indicative of silicon centers with geminal hydroxyl groups, is barely detectable as a shoulder in the spectra obtained by Maciel and Sindorf.

To model a trimethylsilyl group attached to a surface phosphate hydroxyl group it was necessary to react silica with excess phosphate forming a phosphate surface around the silica base. The success of this synthetic phosphate surface was evident in the ^{29}Si NMR spectra (Figs. 2 and 3). In addition to the reduction in the signals at −90 and −100 ppm associated with surface Si–OH groups, the TMS-derivatized material shows no signal at 13 ppm from TMS–O–Si groups. Instead a signal at 26 ppm appears, downfield from the TMS–O–Si resonance. This downfield shift is indicative of a decrease in shielding which is expected due to the higher electronegativity of phosphorus compared to silicon. A resonance at −213 ppm was also observed and believed to arise from the formation of the phosphate surface on silica gel; however, we have no explanation for this resonance at this time.

The spectra of the HMDS reaction product with alumina were found to be dependent on the sample pretreatment. Calcination at 600°C followed by rewetting and recalcining at 200°C, then reaction with HMDS, gave a material having a single resonance at 2 ppm. Without rewetting, a second, broader, resonance appeared at 23 ppm (Fig. 4). This second resonance can be assigned to a by-product of reaction with HMDS since it does not appear if the silating agent is changed to trimethylsilyl ethoxide.

The spectra of silated aluminophosphates, in which the bulk P/Al ratio was made to vary between 0 and 0.9, are shown in Fig. 5. In general, these spectra show two, well-behaved signals which we assign to P–O–TMS and Al–O–TMS surface species. The signals from the trimethylsilyl groups attached to aluminum hydroxyls appear between 0 and 4 ppm and those from the trimethylsilyl groups attached to phosphorus hydroxyls appear between 22 and 26 ppm, which agree well with our reference data in Fig. 2. The narrow ranges found for these trimethylsilyl groups demonstrate the usefulness of this technique for characterizing aluminophosphates. Note also that the intensity of the two signals varies according to the P/Al ratio of the support.

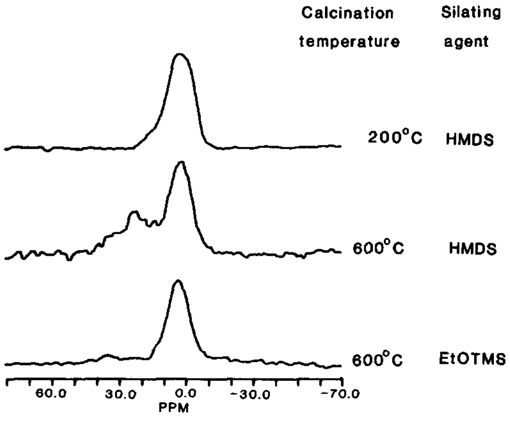


FIG. 4. ^{29}Si CP/MAS NMR spectra of the reaction products of alumina and hexamethyldisilazane or ethoxytrimethylsilane.

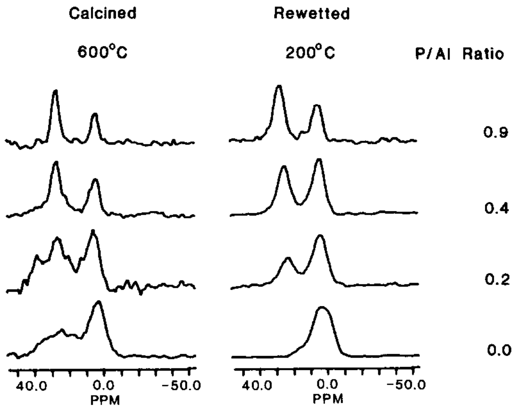


FIG. 5. ^{29}Si CP/MAS NMR spectra of the reaction products of aluminophosphates with hexamethyldisilazane.

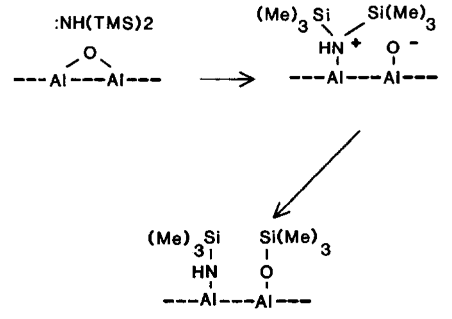
As with alumina itself, the aluminophosphates with low P/Al ratio and calcined at 600°C show evidence of a by-product which appears as a broad resonance near 23 ppm. This obviously biases the P/Al ratio measured from the spectra as the resonance from this by-product cannot be separated from the P–O–TMS signal. Rewetting of the aluminophosphates previous to reaction with HMDS again seems to suppress or eliminate this by-product.

The by-product is best explained by reaction of HMDS at Lewis acid sites on the surface of the alumina and aluminophosphates as indicated in Scheme I. Lewis acid sites in alumina are known to be associated with active Al–O–Al linkages on the surface (*1*). Adsorption of HMDS onto this type of Lewis acid site followed by subsequent reaction of the complex with the adjacent oxide ion would form two types of TMS groups, one bound to the surface via an NH (23 ppm) and the second bound to the surface via an oxygen (2 ppm).

The broad nature of the signal at 23 ppm is further evidence that it arises from an Al–NH–TMS structure. The major isotope of nitrogen is ^{14}N, which has a spin quantum number of 1, and is thus a quadrupolar nucleus. If the internuclear distance is sufficiently small and the nitrogen center is asymmetric, dipolar coupling between the nitrogen quadrupole and the silicon will result in a broadened ^{29}Si NMR signal.

The broadening of the signal at 23 ppm may also result from dipolar coupling of an aluminum quadrupole with the silicon nuclei. However, the signal at 2 ppm, from TMS–O–Al groups, shows no evident broadening from dipolar coupling. Since it is unlikely that HMDS reacts with aluminum to form a direct silicon/aluminum bond giving strong dipolar coupling, the signal at 23 ppm most probably arises from the Al–NH–TMS group.

Note in the 600°C calcined samples in Fig. 5 that the broad resonance at 23 ppm, from the Al–NH–TMS group, gradually decreases in favor of a sharper resonance at 26 ppm from the P–O–TMS group. This suggests a decrease in Lewis acid sites with higher P/Al ratios, in agreement with other workers (*4*). The resonance from the Al–NH–TMS group is not detected in the samples rewetted and calcined at 200°C, which is reasonable since the Lewis acid sites will be eliminated after rewetting provided that the calcination temperature is sufficiently low (Fig. 5). The spectrum of the reaction product of HMDS with alumina (P/Al = 0.0) is especially convincing since there is no P–O–TMS signal to obscure the region around 23 ppm. If the nitrogen-attached species is present in these rewetted samples, it is below our detection limits.



SCHEME I. Mechanism for reaction of hexamethyldisilazane with Lewis acid sites on the surface of alumina.

TABLE 1

Phosphorus to Aluminum Ratios Obtained from the ^{29}Si CP/MAS NMR Spectra of the Reaction Products of Hexamethyldisilazane and Aluminophosphates

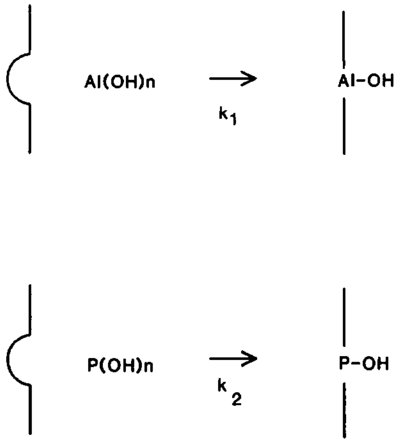
Calcined[a] 600°C	Rewetted 200°C	Bulk P/Al ratio
1.7	1.6	0.9
2.0	0.8	0.4
1.6	0.6	0.2
0.8	0.0	0.0

[a] Includes Lewis acid sites.

The resolution of these spectra is sufficient to obtain a phosphorus to aluminum ratio of the two types of hydroxyls. If one assumes that the reaction rates of HMDS with P–OH and Al–OH are comparable, the integration of each signal gives the concentration of each OH type. These values are listed in Table 1 for samples calcined at 600 and 200°C. Surprisingly, the P/Al ratios thus calculated were significantly higher than expected from the known bulk P/Al ratio. This is especially clear in the 200°C series, where integration is not confused by the overlapping signal at 23 ppm from the nitrogen-attached species. Differences in cross-polarization rates can be disregarded since both signals arise from trimethylsilyl groups with identical geometry between the silicon and the hydrogen nuclei involved in the cross-polarization experiment.

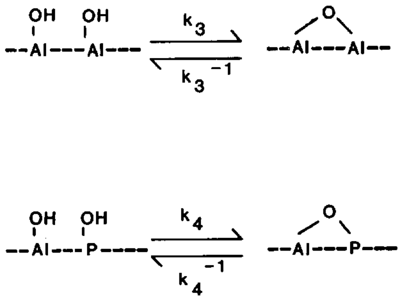
It is unclear whether the surface really contains more phosphate than the bulk. It is not apparent in the infrared spectrum of surface OH groups (*4*), and neither has X-ray photoelectron spectroscopy (XPS) confirmed this trend. In studies from this laboratory on these same supports, XPS-determined P/Al values (which probably penetrate to 20 A) were identical to the bulk values.

There are several possible explanations for this discrepancy in the observed P/Al ratio. The mechanism of formation of these aluminophosphates may preferentially place the P–OH centers in a more accessible position at the surface. In terms of the generalized mechanism in Scheme II, the condensation of aluminum centers with the growing crystal (k_1) would be faster than the condensation of phosphorus centers (k_2).

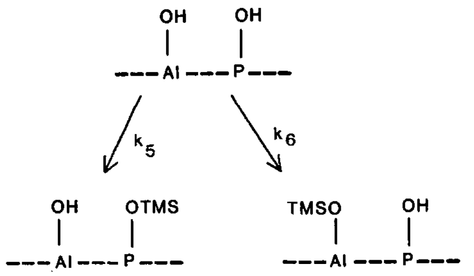


SCHEME II. Condensation of aluminum centers and phosphorus centers with a growing crystal of aluminophosphate.

Alternatively, as shown in Scheme III, the loss of water from adjacent Al–OH groups might be more facile than that from adjacent Al–OH and P–OH groups ($k_3 > k_4$). Calcination would thus preferentially deplete the concentration of aluminum hydroxyl groups, leaving a nearly equal concentration of aluminum and phosphorus hydroxyl groups at the surface. Rewetting, of course, would tend to occur at the more reactive sites, i.e., $k_4^{-1} > k_3^{-1}$.



SCHEME III. Reaction scheme for dehydration of aluminophosphate surfaces.



SCHEME IV. Competitive reaction of silation of aluminophosphate surface.

A third explanation involves the reaction rates of HMDS with the two types of surface hydroxyl groups (Scheme IV). In this case, reaction of HMDS with phosphorus hydroxyl groups would be faster than reaction with Al–OH groups (i.e., $k_5 > k_6$). The end result would be a surface where phosphate TMS groups dominate provided that Al–OH groups next to the P–O–TMS groups were sterically hindered and would not react.

Whatever the cause, the result is an effective surface P/Al ratio similar to a material with much higher P/Al bulk composition, especially after calcination at 600°C. This behavior has also been observed when these aluminophosphates were used as supports for ethylene polymerization catalysts (*28*, *31*). The polymers obtained from these catalysts were usually bimodal in molecular weight distribution demonstrating the chromium's attachment to the two types of hydroxyls. However, the contribution from the P–O–Cr species was usually disproportionately high compared to that from the bulk composition. The NMR data are consistent with this interpretation and suggest that the HMDS reactions at the surface of aluminophosphates provide a good model, being very similar to the reactions involved in placing catalyst systems on the surface of these supports.

Doubly Attached Species (DMS)

Another relevant consideration is the physical location of the two types of hydroxyl groups, i.e., alternating P–OH and Al–OH or regions where one or the other type of hydroxyl groups predominate. The spectra of DCDMS reaction products shed some light on this question. Again several standard surfaces with a single type of hydroxyl group were examined first.

The reaction product with silica gel calcined at 200°C gives three resonances at 7, −4, and −15 ppm (Fig. 6) identical to the resonances noted by Maciel (*18*). These resonances were assigned to the mono-reaction product, the hydrolyzed mono-reaction product, and the di-reaction product, respectively. The structures associated with each of the reaction products are shown in Fig. 7. The presence of the hydrolyzed mono-reaction product was surprising since we carried out the derivatization and NMR spectroscopy under anhydrous conditions. Possibly some calcination occurred at the surface of the silica gel during derivatization which generated H_2O *in situ*. The water then reacted with the mono-reaction product to generate the hydrolyzed mono-reaction product.

On the basis of the previous behavior of trimethylsiloxyl groups, one might expect a 10 ppm upfield shift when replacing a surface silicon center with an aluminum center. Similarly, replacement of a silicon center by a phosphorus center should shift the resonance approximately 10 ppm down-

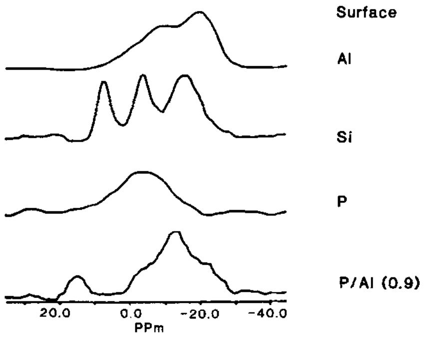


FIG. 6. ^{29}Si CP/MAS NMR spectra of the reaction products of different surfaces with dichlorodimethylsilane.

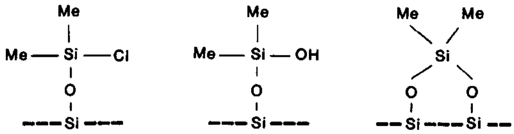


FIG. 7. The three possible reaction products of dichlorodimethylsilane with silica gel.

field. Thus, the mono-reaction product of DCDMS with an alumina surface should appear 10 ppm upfield of the signal found for this same structure in silica, at approximately −3 ppm. The di-reaction product of DCDMS with alumina would be expected to give a signal around −35 ppm since two silicon centers are replaced with two aluminum centers. Similarly the mono-reaction product with a phosphate surface should give rise to a signal at 17 ppm and the di-reaction product at 5 ppm.

The spectrum of the DCDMS reaction product with 200°C alumina shows two major signals, at −6 and −18 ppm. The former can be assigned to the mono-reaction product. However, the latter signal cannot be assigned to the di-reaction product without first considering the possibility that it arises from hydrolysis of the mono-reaction product to form Al–O–$SiMe_2OH$. In comparison, the spectrum obtained from the reaction of diethoxydimethylsilane (DEDMS) with alumina also shows two signals, at −13 and −20 ppm. In this case the signal from the mono-reaction product (−13 ppm) should be comparable to the hydrolyzed mono-reaction product of the previous case since substitution of an OH for an OR group has a relatively small effect (*29*). In addition, the signal around −20 ppm appears in both the DCDMS and the DEDMS reaction products and since both samples were prepared under anhydrous environments, it is quite reasonable to assign this signal to the di-reaction product, i.e., bridging a dimethylsiloxane group.

The spectrum of the DCDMS reaction product with a phosphate surface shows only one major resonance at −4 ppm. This is 20 ppm upfield from where the mono-reaction product would be expected and 10 ppm upfield from the di-reaction product. However, the previous results with alumina indicated that the first aluminum for silicon substitution is more effective than the second substitution which has little or no effect. Assuming the substitution of the second phosphorus center for silicon also has little effect, the signal at −4 ppm can be assigned to the di-reaction product of DCDMS with the phosphate surface. This is reasonable since all other possible products would be expected to give signals further downfield than the di-reaction product.

The spectra of the DCDMS reaction products with aluminophosphate surfaces with high P/Al ratio (0.9) show a major resonance at −12 ppm with shoulders at −5 and −20 ppm. A fourth signal appears far downfield at 16 ppm. The two shoulders can be assigned to the structures found in the spectrum of the reaction product with alumina, namely the mono- and di-reaction products. The signal at −5 ppm probably contains additional contributions from the di-reaction product with a phosphate surface. The signal at 16 ppm can be assigned to the mono-reaction product with a phosphorus hydroxyl group. This latter signal was not detected in the reaction of DCDMS with the phosphate surface.

The major resonance can be assigned to a di-reaction product with the aluminophosphate surface, i.e., a dimethylsiloxane-bridged structure. The three different types of bridged species, Al/Al, Al/P, and P/P, appear at −20, −15, and −4 ppm, respectively. Thus the major resonance at −12 ppm can be assigned to a dimethylsiloxyl bridge between aluminum and phosphorus. Clearly this indicates that the aluminum and phosphorus hydroxyl groups are spatially located next to one another. The surface of aluminophosphate is thus composed of predominately alternating aluminum and phosphorus hydroxyl groups. However, because some Al/Al and P/P bridging is present, the surface is not homogeneous.

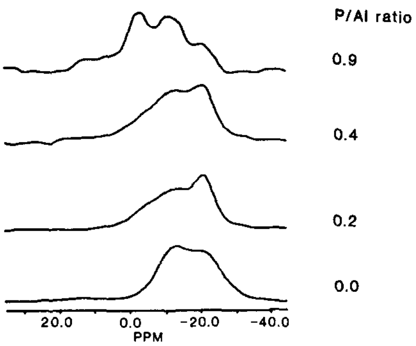


FIG. 8. ^{29}Si CP/MAS NMR spectra of the reaction products of aluminum phosphates with diethoxydimethylsilane.

The reaction of aluminophosphates with DEDMS should follow the behavior of the DCDMS reaction. However, in this case the presence of mono-reaction products with a dimethylsilane group bound to one oxygen and one chlorine is obviously impossible. The spectra obtained from the DEDMS reaction products with aluminophosphates are shown in Fig. 8. Aluminophosphates with low P/Al ratios would be expected to contain a predominance of Al/Al neighboring hydroxyl groups and thus little P/Al bridging structures. However, for the low P/Al samples, the spectra show two major resonances at −14 and −20 ppm from the alternating P/Al and Al/Al bridging dimethylsiloxane groups. A shoulder at −5 ppm from P/P bridging dimethylsiloxane groups is barely detectable. However, as was the case for the DCDMS reaction products, aluminophosphate with high P/Al ratio clearly shows P/P bridging dimethylsiloxane groups as well as P/Al and Al/Al bridges.

IV. CONCLUSION

The presence of both P–OH and Al–OH on aluminophosphate surfaces is easily detected using ^{29}Si CP/MAS NMR of the silated surfaces. The P/Al ratio obtained at the surface for the two types of silanes differs significantly from the P/Al ratio of the bulk of the material. This suggests a dominance of the phosphate hydroxyl in surface reactions, i.e., an effective P/Al ratio at the surface greater than the bulk P/Al ratio. The dominance of the phosphate hydroxyl in surface reactions does not necessarily indicate a higher concentration of phosphate hydroxyl groups on the surface. A faster reaction rate in the derivatization of the phosphate hydroxyls than that of the aluminum hydroxyls could easily form a surface where the derivatized phosphate hydroxyl groups sterically shield neighboring aluminum hydroxyl groups from further reactions.

Calcination of aluminophosphates at 600°C leads to the formation of some Lewis acid sites on the surface, particularly at low phosphate levels. These sites can then react with hexamethyldisilazane to form Al–NH–TMS groups which are also detectable in the ^{29}Si CP/MAS spectra. Rewetting of the calcined material, or calcining at lower temperatures, suppresses the formation of the Lewis acid sites.

The dichlorodimethylsilane reaction products with aluminophosphates show that the predominate bridging dimethylsiloxane groups are between phosphorus and aluminum. Thus, the surface of aluminophosphates is composed primarily of alternating phosphorus and aluminum hydroxyl groups; however, the presence of Al/Al and P/P dimethylsiloxane bridges demonstrates that the surface is not completely homogeneous. As expected, as the P/Al ratio of aluminophosphate decreases, the concentration of Al/Al neighboring hydroxyl groups increases.

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