(27.6); Figure 4, acetone/chloroform/benzene 19.7:47.2:33.1 with 4.5% $CDCl_3$ in sample a and 1.2% C_6D_6 in sample b (relative to the total weight 2.5 and 0.5%, respectively). A 16 × 2048 data matrix was recorded and zero-filled to 64 × 4096 prior to transformation. Time intervals were Δ_1 = 17.85 ms, Δ_2 = 8.92 ms, the relaxation delay was 2 s, acquisition time was 0.17 s, and 512, 1280, and 1024 transients, respectively, were collected.

The polarization transfer ^{13}C spectrum of Figure 5a was obtained with the UPT pulse sequence[12] with $\theta = \pi/6$ = 31.5 μs and $\tau = 1/2J(^{13}C,^2H)$ = 25 ms; a 10 s relaxation delay was chosen to achieve more accurate integration results. The total experimental time was 30.9 h. For the two-dimensional shift correlation (Figure 5b) a sample of 100 mg of the alcohol mixture **3a–c** in C_6F_6, which also served for the ^{19}F lock, was used (concentration 0.4 M). Sweep widths were 100 Hz (F_1) and 724.6 Hz

(F_2), respectively, with quadrature detection in both dimensions and ^1H and/or ^2H decoupling as above. The t_2 acquisition time was 0.353 s, the relaxation delay was 2.647 s, and the number of transients in t_2 was 1000. The original 16 × 512 data matrix was zero-filled to 64 × 1024; a Gauss-type filter function matched for sensitivity enhancement was used in t_2 and a sine bell function in t_1. The total experimental time was 15 h.

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Acid Sites in Zeolite Y: A Solid-State NMR and Infrared Study Using Trimethylphosphine as a Probe Molecule

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Abstract: ^{31}P MAS-NMR spectra of trimethylphosphine adsorbed on H–Y zeolites have been obtained from samples calcined at 400–700 °C. For a 400 °C calcined sample, the spectrum was dominated by a resonance at ca. −3 ppm which is assigned to $[(CH_3)_3P–H]^+$ complexes that arise from chemisorption at Brønsted acid sites in the zeolite; an infrared band at 2485 cm^{-1} is also attributed to this species. When this sample was degassed at 80 °C for 0.5 h, intense dipolar-derived spinning sidebands and a J coupling of ~550 Hz characterized the spectrum. By contrast, the spectrum of a sample degassed for 1 h at 300 °C showed a well-resolved J coupling but very weak sidebands. These results suggest the presence of at least two $[(CH_3)_3P–H]^+$ species: an immobilized complex, attributed to coordination with hydroxyl protons, and a complex which shows a high degree of motion on the NMR time scale. This latter species is stable to desorption at 300 °C. ^{31}P MAS-NMR spectra from samples calcined at 500 °C and above showed additional resonances in the region from ca. −32 to −58 ppm when trimethylphosphine was chemisorbed. Comparison of these shifts with model systems suggests that they arise from chemisorption to Lewis sites. The −58 ppm resonance can be ascribed to the presence of Al_2O_3 clusters in the zeolite at high calcination temperatures, in support of previous studies. The 500 °C calcined sample showed a resonance at −10 ppm that exhibited weak proton coupling; this resonance is attributed to a site where trimethylphosphine is coordinated to both a Lewis and a Brønsted acid site. The present study introduces trimethylphosphine as a sensitive NMR probe molecule for acidity measurements on catalytic surfaces.

The acid form of zeolites is important in a variety of catalytic reactions including hydrocarbon cracking, isomerization, and alkylation. In order to characterize these materials, one would like to know the strength and distribution of acid sites, as well as the origin of particularly strong acidity. To determine acidity, various methods have been employed such as titrating to a particular end point[1] or measuring the heat of adsorption of ammonia.[2] The infrared spectra of probe molecules such as pyridine and other bases have been used to provide evidence for both Brønsted and Lewis acid sites,[3] but distinctions within these rather broad classifications cannot generally be made.

More recently, ^{15}N NMR has been used to characterize acid sites on zeolites and other aluminosilicates.[4-7] Haw et al.,[7] for example, have shown that the chemical shift of ^{15}N in pyridine may be used to distinguish between Brønsted and Lewis sites. Moreover, *n*-butylamine is a stronger base which displaces pyridine from Brønsted sites and, at higher coverages, from Lewis sites. Estimates of the amount of Brønsted acidity can be obtained from the equivalents of *n*-butylamine required to completely displace pyridine from the Brønsted acid sites.

We have reported that trimethylphosphine reacts with protons in H–Y zeolite to form a $[(CH_3)_3P–H]^+$ complex.[8] The ^{31}P cross-polarized magic-angle spinning NMR (CP/MAS-NMR) spectrum of this species is characterized by a chemical shift of −2 ppm. In the absence of proton decoupling the spectrum consists of a doublet ($J \cong 550$ Hz) centered at −2 ppm, with intense, dipolar-derived spinning sidebands that are also split into doublets. Evidence for the formation of trimethylphosphonium ions in H–Y zeolite also comes from the infrared study of Schoonheydt et al.[9]

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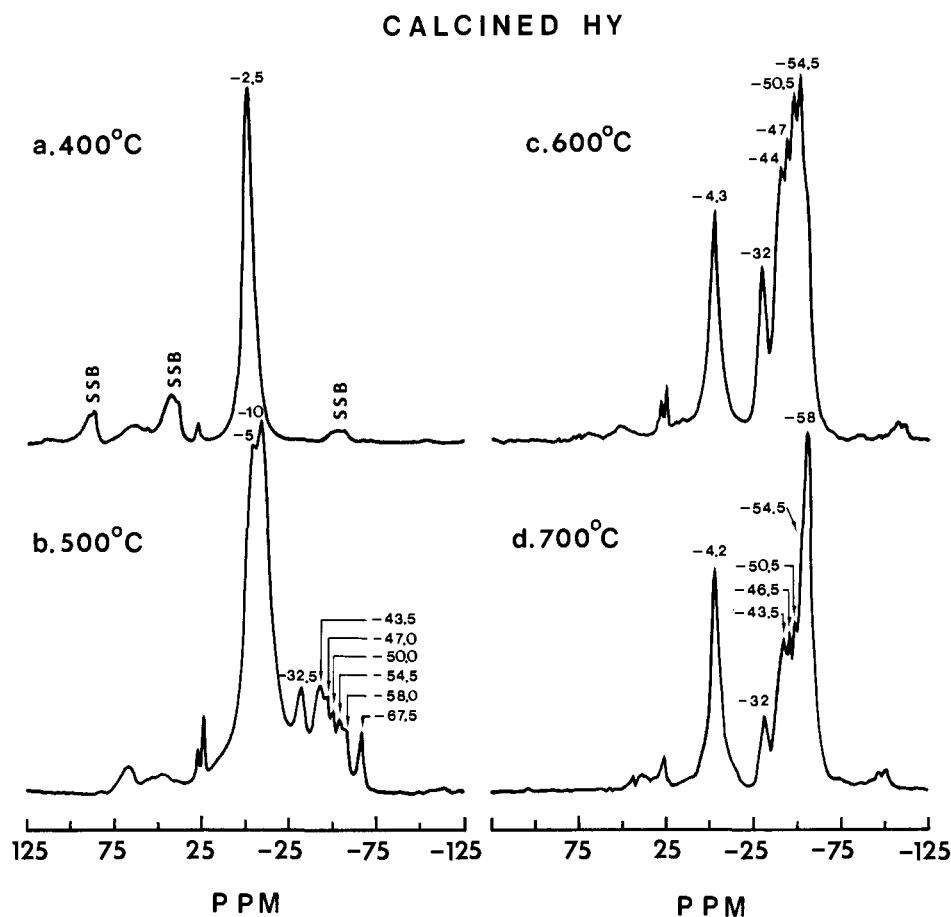
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CALCINED HY

Figure 1. Effect of calcination temperature on the ^{31}P MAS-NMR spectrum $(CH_3)_3P$ in a H–Y zeolite; all samples degassed at 80 °C (1 h). Sample calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C. 90° pulse excitation; recycle delay = 10 s. The chemical shift of the broader resonance is rounded to the nearest 0.5 ppm.

In the present study, we have focused on the transformations in acid sites that occur in a H–Y zeolite upon calcination at successively higher temperatures. The evolution of acid sites in the temperature range 400–700°C is important in understanding the effect of calcination temperature on catalytic behavior.[10] The emphasis has been on the type of acid sites that are formed rather than on the concentration of these sites. The latter aspect will be the subject of future investigations.

The present experiments benefit substantially from the excellent sensitivity and the large range of chemical shifts of the ^{31}P nucleus. NMR offers some distinct advantages over other spectroscopic approaches in that it can be used in a quantitative fashion without ambiguities such as differences in extinction coefficients. It can also yield information on the dynamics of adsorbed molecules (see below).

Experimental Section

NMR Experiments. Hydrogen–Y zeolites were prepared in small quantities (0.5 g) by slowly heating a NH_4Y zeolite (Linde, No. Y-6z, 373856) under vacuum to temperatures from 400 to 700°C. The zeolites, having a bed depth of ~4 mm, were held at the maximum temperature for 2 h. Trimethylphosphine (Strem) was adsorbed at 25 °C from the vapor phase (20 torr) for a period of 2 h. Trimethylphosphine is a useful probe molecule because its kinetic diameter (~5.5 Å) is sufficiently small so that it may diffuse through the 8-Å openings into the large cavities. Excess $(CH_3)_3P$ was removed by heating the sample under vacuum for various times at different temperatures. The sample was transferred to the NMR spinner in a glovebox to minimize contamination with air. To simplify the presentation, we will use the following convention: a H–Y sample calcined at 500 °C, exposed to trimethylphosphine, and then degassed at 80 °C for 1 h will be designated 500°C-HY-80°C(1h).

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The $(CH_3)_3P$ + γ-Al_2O_3 (Catapal SB Alumina) sample was prepared by first degassing the Al_2O_3 at 400 °C for 1 h, adding 400 torr of O_2, and increasing the temperature to 500 °C for 4 h followed by evacuation in vacuo at 500 °C for an additional 2 h. The sample was cooled to room temperature, and 20 torr of $(CH_3)_3P$ was added and allowed to equilibrate for 2 h. The sample was degassed at room temperature for 0.5 h. The $(CH_3)_3P$ + $AlCl_3$ sample was prepared by exposing anhydrous $AlCl_3$ powder (in an evacuated tube) to $(CH_3)_3P$ vapor. The sample was degassed at room temperature and flame-sealed in a glass ampule.

The ^{31}P MAS-NMR spectra were acquired on a Bruker CXP-200 spectrometer by using a Chemagnetics probe. Cross-polarization and 90° pulse methods were used in conjunction with magic-angle spinning and high-power proton decoupling. The 90° pulse time was 6 μs for both ^1H and ^{31}P. Typical spinning rates of 3–4 kHz were employed by using dry nitrogen as the drive gas. Typically, the ^{31}P spectra were easily acquired with only ca. 15 min of signal averaging. Superior NMR sensitivity for ^{31}P derives from the large gyromagnetic ratio and large (100%) natural abundance for this nucleus. In addition, the samples were all characterized by relatively short ^{31}P T_1's (estimated in the range of 1–3 s), enabling rapid, quantitative acquistion of all spectra. Chemical shifts are reported relative to 85% H_3PO_4 by using solid tetramethyldiphosphine disulfide as a secondary reference (downfield peak at +37.86 ppm); negative shifts are taken to be upfield.

**IR Experiments.** Infrared spectra were obtained on self-supporting zeolite wafers (ca. 5 mg/cm^2) that were degassed in a Vycor cell equipped with KCl windows. The procedure was essentially the same as that used to prepare the NMR samples. The $(CH_3)_3P$ was desorbed by heating the zeolite under vacuum at progressively higher temperatures. Spectra was recorded with the sample at room temperature by using a Perkin-Elmer Model 580B spectrophotometer.

Results

NMR Studies: Effects of Calcination. The effects of progressively higher calcination temperatures on the ^{31}P MAS-NMR spectra are shown in Figure 1. The ^{31}P spectrum of the 400°-C-HY-80°C(1h) [Figure 1a] is similar to that reported previously,[8] except that the present sample was degassed for a longer period
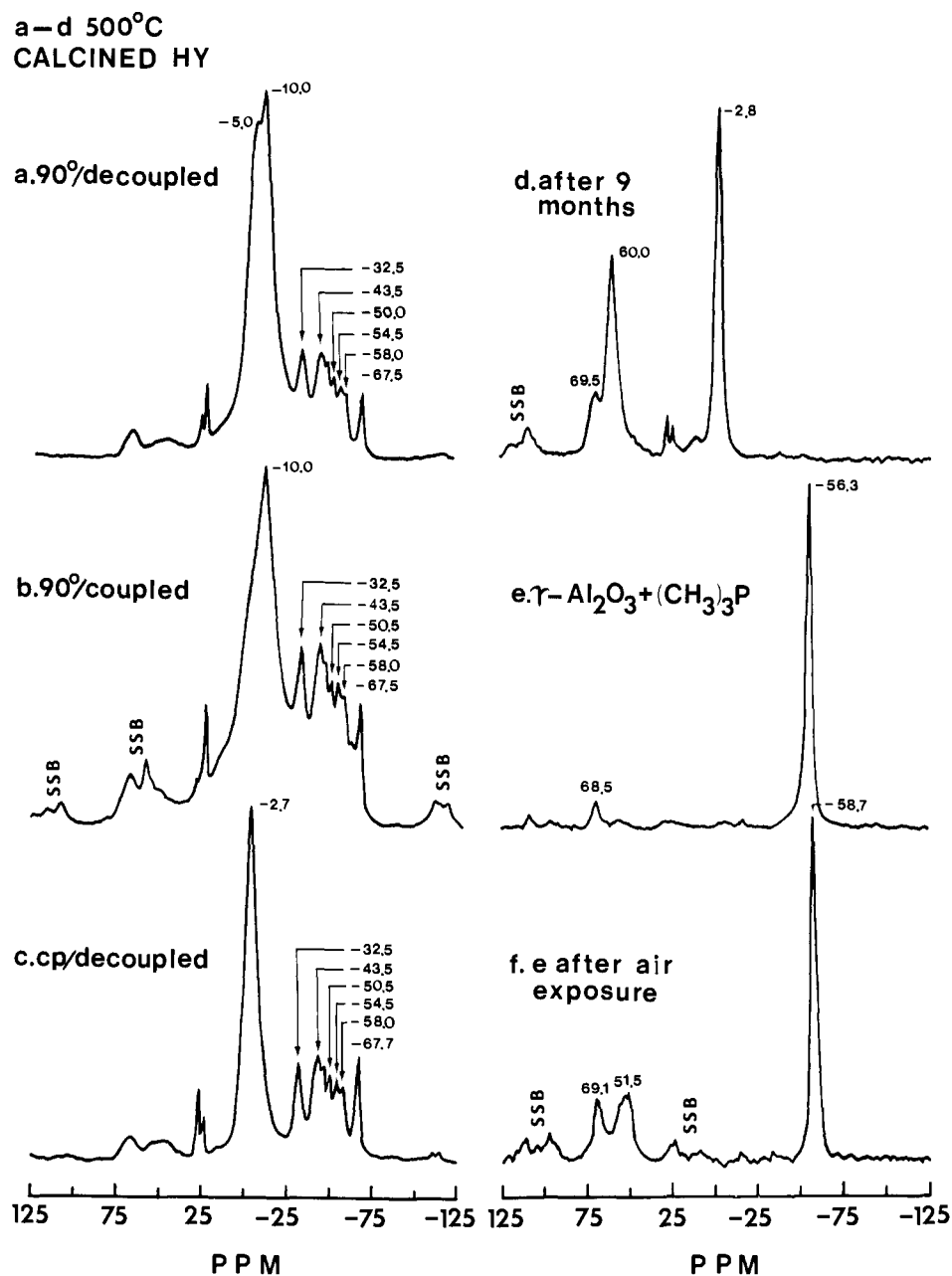
Figure 2. ^{31}P MAS-NMR spectra of $(CH_3)_3P$ in the 500°C-HY-80°C(1h) sample: (a) 90° pulse, proton-decoupled, (b) 90° pulse, proton-coupled, (c) cross-polarization (contact time = 5 ms), (d) 90° pulse spectrum after sample had been left in spinner for 9 months (recycle delay = 2 s, number of scans = 84). ^{31}P MAS-NMR spectra of $(CH_3)_3P$ adsorbed on γ-Al_2O_3 (e and f). (e) 90° pulse spectrum prior to air exposure (recycle delay = 10 s, number of scans = 88). (f) 90° pulse spectrum after sample was exposed to air for 45 min (recycle delay = 10 s, number of scans = 88, vertical gain $\simeq$ 2× gain for spectrum e).

and there is no evidence for physisorbed $(CH_3)_3P$ (δ_P −67). The ^1H-coupled spectrum (not shown) is characterized by a series of intense, dipolar-derived spinning sidebands with poorly resolved J coupling.

After the zeolite was calcined at 500–700 °C, the NMR spectra of the $(CH_3)_3P$ chemisorbed on H–Y samples show additional resonances, having chemical shifts at −32, −44, −47, −50, −54, and −58 ppm, as depicted in Figure 1b–d. For the 500°C-HY-80°-C(1h) and 600°C-HY-80°C(1h) samples, these resonances grow in intensity relative to the group near −2 ppm, although their intensities appear to increase independently of one another. After calcination at 700 °C, the resonance at −58 ppm dominates the spectrum. These new peaks are essentially unchanged in proton-coupled spectra, whereas the intensity of the resonance at −2 to −4 ppm, ascribed to a protonated complex (see below), is markedly decreased.

Proton-decoupled 90° pulse, coupled 90° pulse, and decoupled cross-polarization spectra are reported for the 500°C-HY-80°C-(1h) sample in Figure 2a–c, respectively. The −10 ppm resonance

is broadened in the coupled spectrum but J coupling is not well resolved. From measurement of their frequency separation, the spinning sidebands that exhibit J coupling are associated with a line at ~−2 ppm, not with the line at −10 ppm. The decoupled 90° pulse spectrum indicates that the −10 ppm resonance has the largest intensity relative to the high-field resonances, whereas the −10 ppm resonance appears as only a weak shoulder in the cross-polarization spectrum.

Additional NMR Observations. In a parallel NMR study of $^{15}NH_3$ absorbed in a H–Y zeolite, it was observed that the ^{15}N chemical shift was significantly affected by the presence of water in the zeolite.[11] In an effort to elucidate further the nature of this interaction, a similar study was carried out by using $(CH_3)_3P$ and H_2O. The addition of H_2O vapor to a 400°C-HY-80°C(1h) sample resulted in a slight (~1 ppm) downfield shift of the major resonance of the chemisorbed $(CH_3)_3P$ together with the ap-

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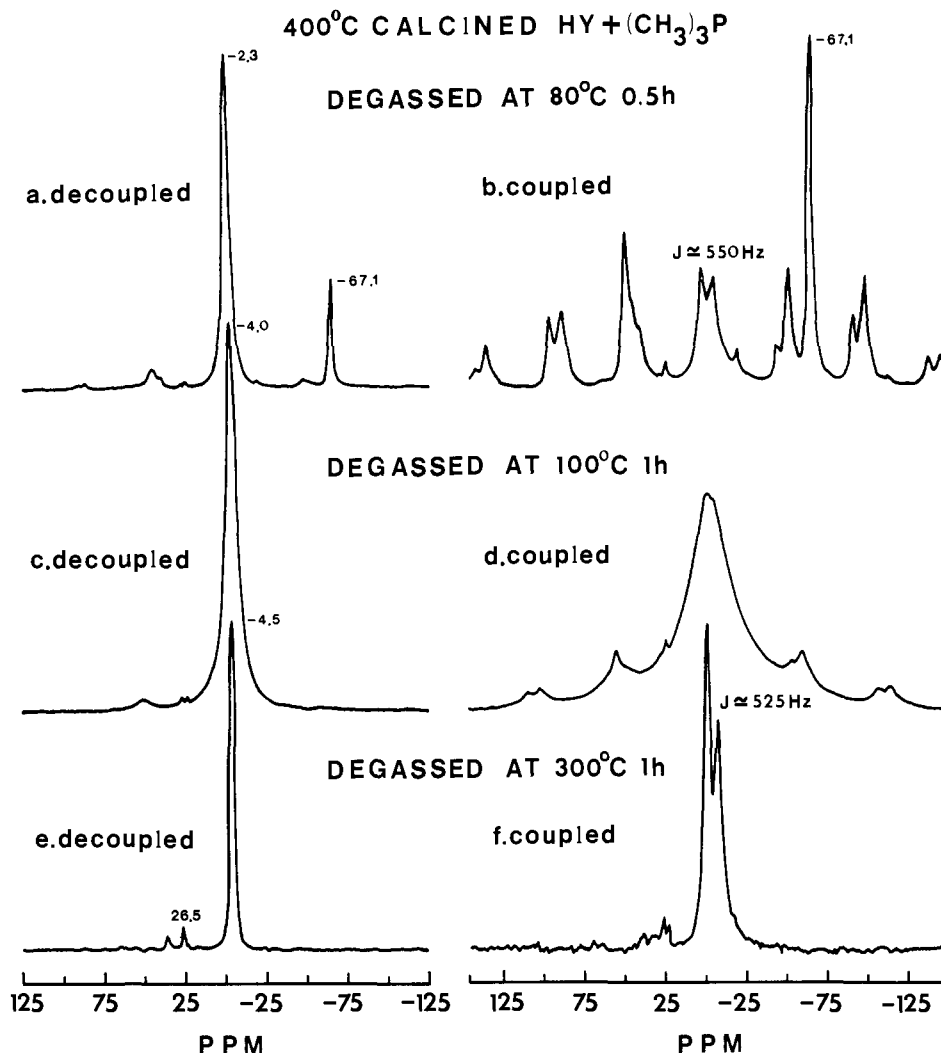
Figure 3. ^{31}P MAS-NMR spectra of $(CH_3)_3P$ in a H–Y zeolite calcined at 400 °C: (a) after $(CH_3)_3P$ desorbed at 80 °C (0.5 h), 90° pulse, proton-decoupled; (b) same as (a) except no proton decoupling; (c) after $(CH_3)_3P$ desorbed at 100 °C (1 h), 90° pulse, proton-decoupled; (d) same as (c) except no proton decoupling; (e) after $(CH_3)_3P$ desorbed at 300 °C (1 h), 90° pulse, proton-decoupled; (f) same as (e) except no proton decoupling.

pearance of a more sharply defined coupled spectrum showing intense, dipolar-derived sidebands.

Low-intensity resonance in the region characteristic of phosphine oxides ($\sim+50$ ppm) were noted in spectra of several of the samples. To elucidate the origin of these species, several samples were exposed to air and their spectra recorded. Spectra e and f of Figure 2 show results from a $(CH_3)_3P + \gamma\text{-}Al_2O_3$ sample before exposure to air and after ~45 min of air exposure, respectively. The -56.3 ppm resonance shifts to -58.7 ppm, and the integrated peak intensity is reduced approximately to half of the original value. Most significantly, there is a substantial increase in spectral intensity at $+51.5$ ppm as a consequence of air exposure.

Figure 2d shows a ^{31}P spectrum of the 500°C-HY-80°C(1h) sample after it had been left in a closed spinner for 9 months; the same sample examined 9 months earlier gave rise to the spectrum displayed in Figure 1b. The resonances between -10 and -58 ppm are clearly absent in the aged sample and are replaced by a pair of intense resonances at $+60$ and $+70$ ppm. These spectral changes are attributed to reaction of some of the chemisorbed trimethylphosphine with O_2 and perhaps moisture resulting from air leakage into the spinner. In addition to these downfield "impurity" peaks, two additional, weak, narrow resonances were detected further upfield at $+23$ and $+26$ ppm in most of the samples.

Model Compounds. ^{31}P solid-state NMR spectra were obtained for $(CH_3)_3P$ adsorbed on anhydrous $AlCl_3$ and on anhydrous $\gamma\text{-}Al_2O_3$. The $(CH_3)_3P/AlCl_3$ spectrum exhibited a pair of broadened resonances at -35 and -42 ppm that are assigned to

Table I. ^{31}P Chemical Shift as a Function of Desorption Temperature

| desorption temp, °C	^{31}P chemical shift of $[(CH_3)_3P\text{-}H]^+$ complex, ppm
25 (0.5 h)[a]	-1.9
80 (0.5 h)[b]	-2.3
80 (1 h)	-3.6
100 (1 h)	-4.0
300 (1 h)	-4.5

[a] $(CH_3)_3P$ adsorbed at 25 °C. [b] Numbers in parentheses refer to time of desorption.

Lewis acid–base complexes. In addition, a resonance attributed to a $[(CH_3)_3P\text{-}H]^+$ complex was observed at -5.7 ppm with $J_{P\text{-}H} \cong 500$ Hz; the resonances assigned to Lewis complexes did not display evidence of J coupling. The proton sites in $AlCl_3$ apparently were formed from water impurities.

The ^{31}P spectrum of $(CH_3)_3P$ chemisorbed on $\gamma\text{-}Al_2O_3$ is shown in Figure 2e. The resonance at -56.3 ppm (no observed J coupling) is assigned to a Lewis acid complex. Additional, weak resonances are detected much further downfield and are associated with oxidation products (see above).

Thermal Desorption Studies. NMR spectra were acquired as a function of the amount of $(CH_3)_3P$ desorbed at progressively higher temperatures. The relative amount of $(CH_3)_3P$ remaining in the zeolite is better determined by the infrared results (see below), but the NMR spectra reveal several interesting points. First, there is a distinct displacement of the chemical shift to higher fields as the trimethylphosphine is removed, as shown in Table

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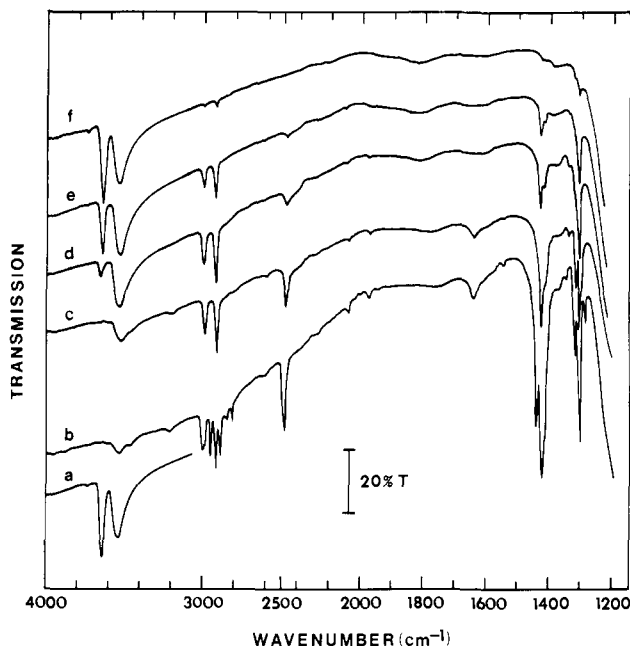
Figure 4. Infrared spectra of $(CH_3)_3P$ in a H–Y zeolite calcined at 400 °C: (a) background spectrum, (b) after $(CH_3)_3P$ desorption at 25 °C, (c) after desorption at 80 °C, (d) after desorption at 200 °C, (e) after desorption at 300 °C, (f) after desorption at 400 °C. Desorption was carried out for 1 h.

I. Second, a more obvious point is the large variation in the intensities of the spinning sidebands—both in the coupled and decoupled spectra—as chemisorbed $(CH_3)_3P$ is removed from the zeolite. This phenomenon is clearly seen in Figure 3 by comparing spectra from the 400°C-HY-80°C(0.5h) (Figure 3a and b) and 400°C-HY-300°C(1h) (Figure 3e and f) samples. The coupled spectrum of the sample degassed at 300 °C shows very weak spinning sidebands; the coupled spectrum of the sample degassed at 80 °C shows intense sideband intensities, as previously reported.[8] Both spectra display well-resolved *J* coupling. The 80 °C degassed sample also gives rise to a peak at −67 ppm attributed to physisorbed $(CH_3)_3P$. Decoupled and coupled spectra for a 400°C-HY-100°C(1h) sample are shown in Figure 3c and d. The isotropic shift occurs at an intermediate value (−3.6 ppm), and the coupled spectrum is broad ($\Delta\nu_{1/2} \cong 2.5$ kHz), displaying only weak sidebands.

IR Studies. The infrared spectra of $(CH_3)_3P$ and hydroxyl bands in a H–Y zeolite closely parallel the results reported by Shoonheydt et al.[9] and will not be described again in detail. The salient features, however, are summarized in the spectra of Figure 4. The characteristic infrared spectrum of a H–Y zeolite is shown in Figure 4a. Calcination at 600 or 700 °C caused a marked decrease in the amplitude of the bands due to hydroxyl and phosphonium ions, but no new infrared bands that might be attributed to $(CH_3)_3P$ coordinated to Lewis sites were detected.

Discussion

Tertiary phosphines are known to form stable complexes with both Brønsted and Lewis acids. In this regard trimethylphosphine is categorized as a "soft" base and therefore, according to Pearson's principle,[12] interacts most strongly with soft acids such as BH_3. Nevertheless, one would anticipate reasonably strong complexes between $(CH_3)_3P$ and "hard" acids such as Al^{3+}, $AlCl_3$, and H^+, providing a favorable basis for use of trimethylphosphine as a probe for acidity on catalytic surfaces.

In a recent communication,[8] we presented ³¹P solid-state NMR evidence for a $[(CH_3)_3P-H]^+$ complex resulting from the interaction of $(CH_3)_3P$ with Brønsted sites in dehydrated H–Y zeolite. In addition to a resonance at −67 ppm, assigned to physisorbed $(CH_3)_3P$, a resonance at −2 ppm was observed and attributed to

a $[(CH_3)_3P-H]^+$ complex on the basis of (1) the very close similarity to the chemical shift of −2.8 ppm for $[(CH_3)_3P-H]^+$ in solution[13] and (2) the observed ¹H coupled doublet with $J \sim 550$ Hz.[14] The appearance of a well-resolved ¹H *J* coupling in a solid is unusual but can be observed in such materials as a consequence of weak ¹H–¹H direct dipolar coupling. More typically, ¹H–¹H direct dipolar coupling is the dominant spin interaction and renders the spin Hamiltonian homogeneous. Unattainably fast spinning speeds must be employed to resolve ¹H *J* coupling in such typical cases.

The ³¹P spectrum of 400°C-HY-80°C(1h) (Figure 1a) displays a strong resonance at −2.5 ppm which is assigned, in agreement with our previous work, to a $[(CH_3)_3P-H]^+$ complex arising from interaction with Brønsted sites in the zeolite. This assignment is supported by the observation of intense, dipolar-derived spinning sidebands in the ¹H-coupled spectrum. The absence of well-resolved *J* coupling and the increased line width ($\Delta\nu_{1/2} \cong 5.7$ vs. 4.7 ppm from our previous study) suggests a heterogeneity of Brønsted environments or may reflect the presence of motional broadening (see below). Infrared spectra show bands at 1300–1450, 2485, and 2900–3000 cm^{-1} when trimethylphosphine is chemisorbed on H–Y zeolite. Schoonheydt et al.[9] concluded that the 2485-cm^{-1} band was due to the $[(CH_3)_3P-H]^+$ ion, consistent with the NMR results presented here.

From the infrared spectra of adsorbed pyridine, it is known that the concentration of Brønsted acid sites decreases rapidly as H–Y zeolite is calcined at temperatures above 500 °C. This has been ascribed to dehydroxylation of the Brønsted sites and results in the formation of Lewis sites. There is a paucity of ³¹P NMR data concerning relevant Lewis acid complexes of $(CH_3)_3P$. Cowley and Damasco[15] have reported a ³¹P shift of −1.8 ppm for the soft acid/base complex, $(CH_3)_3P-BH_3$ (neat $(CH_3)_3P$ has a chemical shift of −62.8 ppm). Other complexes of $(CH_3)_3P$ can appear even further downfield, e.g., $(CH_3)_3P-PCF_3$ (+12.7 ppm)[16] and (C-$H_3)_3P-PF_5$ (+24 ppm).[17] A ³¹P study of $(CH_3)_3P/AlCl_3$ complexation in dichloromethane has indicated the presence of 1:1 (−47 ppm) and 2:1 (−51 ppm) adducts in fast exchange with free $(CH_3)_3P$ (−66 ppm in CH_2Cl_2);[18] Lewis complexes with *solid* $AlCl_3$ apparently result in somewhat larger coordination shifts (this study).

The present ³¹P results for $(CH_3)_3P/AlCl_3$ and $(CH_3)_3P/\gamma$-Al_2O_3 suggest that $\sim$−35 to $\sim$−56 ppm is probably a more appropriate range for Lewis complexes with Al^{3+}, a hard acid. However, in view of the further downfield shifts of complexes such as $(CH_3)_3P-BH_3$, it is possible that this shift range should be further extended in the downfield direction. Thus, it is important to verify assignments to Brønsted or Lewis sites by the acquisition of ¹H-coupled ³¹P spectra.

We assign the −32 to −58 ppm resonances noted in the spectra from the 500°C-HY-80°C(1h), 600°C-HY-80°C(1h), and 700°C-HY-80°C(1h) samples (Figure 1b–d) to Lewis acid–base complexes. This assignment is supported by the lack of evidence for substantial ¹H direct or indirect dipolar interactions in the coupled spectra and is consistent with the expected range of chemical shifts for Lewis complexes with Al^{3+} (see above). The formation of Lewis acid sites upon calcination at 500 °C and above is in agreement with previous infrared studies.[19] Apparently, the Lewis-bound species detected by MAS-NMR do not exhibit a sufficient wavenumber shift to be resolved in the infrared spectra.

Since distinct, well-resolved resonances are observed in all the spectra reported here, $(CH_3)_3P$ cannot be jumping between the *observed* sites unless it is at a slow rate compared to the chemical-shift differences ($\sim$5 kHz); however, rapid exchange between

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two or more *unobserved* sites could, of course, occur, giving rise to average resonances in the spectrum. It is important to note that eradication of possible dipole–dipole couplings between ^{31}P and ^{27}Al nuclei by magic-angle spinning is not assured because of a nonzero ^{27}Al quadrupole moment. The resulting ^{31}P spectrum could exhibit a complex splitting pattern that is dependent on the details of the ^{27}Al quadrupole-coupling tensor (unknown), the internuclear distance, and the applied magnetic field[20] (the effect is greatest at low magnetic fields). Splittings of 100–200 Hz have been noted in ^{13}C spectra of ^{13}C–^{14}N pairs in solids[20] but may be absent in some systems due to "self-decoupling".[21] Although we cannot, at present, rule out possible quadrupole-related splitting in the Lewis region, the near invariance in peak *positions* and the apparent independence of peak *intensities* for the present samples together with a preliminary comparison of spectra taken at 4.7 and 8.5 T from a 550 °C calcined sample (not reported here) suggest that these effects are not large. (Large ^{27}Al–^{31}P internuclear distances ensure that this is not an important effect for the Brønsted region.) Further, quadrupolar-induced splitting is clearly absent in the ^{31}P spectrum of the $(CH_3)_3P$–γ-Al_2O_3 complex and has not been invoked to explain results in a number of recent ^{1}H MAS studies,[22] although ^{1}H–^{27}Al dipole–dipole coupling would be expected to be comparable to ^{31}P–^{27}Al coupling in aluminosilicates.[23] Nevertheless, some caution in attributing all the observed resonances as chemical shifts is needed until more higher field results become available.

The origin of the Lewis acid sites in zeolites is not presently clear. In earlier work Uytterhoeven et al.[24] proposed that dehydroxylation resulted in tricoordinate lattice aluminum; however, on the basis of high-resolution solid-state ^{1}H and ^{27}Al NMR, Freude et al.[22b] have concluded that dehydroxylation in the neighborhood of a lattice aluminum atom is always accompanied by its release from the framework. They also presented evidence that Al_2O_3 clusters, which cannot be rehydrated, are formed during deep or shallow bed calcinations at high temperature. The clusters are thought to be deposited inside secondary pores. Evidence for aluminum oxide clusters in ultrastable zeolites is also derived from the experiments of Lohse et al.[25]

The appearance of a multitude of ^{31}P resonances associated with Lewis sites in our high-temperature calcined samples indicates that there are a number of different coordination sites present. Although these results do not provide direct evidence in support of the proposal by Freude et al.,[22b] they are consistent with the concept of a heterogeneous Lewis site distribution in calcined H–Y zeolites. The appearance of the −58 ppm peak as the dominant resonance for the 700°C-HY-80°C(1h) sample and its close agreement with the chemical shift for $(CH_3)_3P$ chemisorbed on γ-Al_2O_3 provide independent evidence in support of the conclusion that Al_2O_3 forms as a high-temperature dehydroxylation product from H–Y. The increase in the −58 ppm peak intensity with temperature suggests that Al_2O_3 formation is greater at high temperature, in agreement with the results of Freude et al.[22b]

One of the more interesting features of the present study is the appearance of the resonance at −10 ppm following calcination at 500 °C (Figure 1b). This is the approximate temperature at which strong acidity for catalytic cracking begins to develop.[3,10] The behavior of the −10 ppm resonance in the coupled and cross-polarization spectra suggests that the trimethylphosphine species exists as a coordination complex with both a proton (Brønsted

site) and an exposed aluminum atom (Lewis site). If one accepts the dehydroxylation mechanism of Kühl,[26] Freude et al.,[22b] and others,[27] i.e., no structural tricoordinated aluminum is present, this species could exist as the following complex:

A
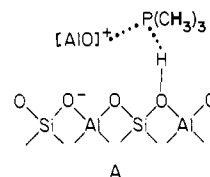
Such a coordination site would be expected to form while there is still a high concentration of hydroxyl groups in the zeolite.

Thermal Desorption. The infrared bands at 3550 and 3650 cm^{-1} for the H–Y zeolite have been assigned to hydroxyl groups in which acidic protons are bonded to structural oxygen atoms. Earlier work suggests that the proton associated with the band at 3550 cm^{-1} extends into the small cavity and that the proton associated with the 3650-cm^{-1} band extends into the large cavity.[28] Clearly upon adsorption at 25 °C, $(CH_3)_3P$ reacts with both protons (Figure 4b), even though it is too large to enter the small cavity. The interaction of a large molecule such as $(CH_3)_3P$ with the seemingly inaccessible hydroxyl group at 3550 cm^{-1} may, at first glance, seem surprising but can be rationalized on the basis of the mobility of the protons in H–Y$^{29-31}$ (see below).

The infrared spectrum of the 400°C-HY-300°C(1h) sample, Figure 4e, suggests that most of the hydroxyl band at 3550 cm^{-1} has been restored by degassing at 300 °C; however, a significant reduction in intensity remains in the band at 3650 cm^{-1}. Thus, it appears that the $(CH_3)_3P/3550$-cm^{-1} hydroxyl complex undergoes nearly complete dissociation at 300 °C, but the $(CH_3)_3P/3650$-cm^{-1} hydroxyl complex is incompletely dissociated. These results are in agreement with the infrared study of Schoonheydt et al.[9] Hughes and White[32] noted a similar trend upon desorption of piperidine from H–Y. They observed that the 3550-cm^{-1} band was partially restored at 200 °C, but desorption at 400 °C was necessary to restore the 3650-cm^{-1} band. Since higher temperatures were required to remove the base from the 3650-cm^{-1} hydroxyl, this group was associated with the stronger Brønsted acid site.

From the above, we conclude that the $(CH_3)_3P$ complex seen in the spectrum of the 400°C-HY-300°C(1h) sample ("type I"; δ_P −4.5) arises from interaction with the 3650-cm^{-1} hydroxyl group. Since substantial sideband intensity is absent from the proton-coupled spectrum, we must also conclude that the proton is completely abstracted by the trimethylphosphine to form a discrete phosphonium ion which is engaged in rapid rotational and, most likely, translational jumps at room temperature. The rotational jump rate must substantially exceed ∼8 kHz, the estimated magnitude of the ^{31}P–^{1}H dipole–dipole coupling.[8] It is possible that the asymmetry in the proton-coupled doublet reflects an additional, unresolved component or arises as a consequence of magic-angle spinning modulation of residual anisotropies.[8]

Since the magnitude of the measured J coupling is in the normal range found for $[(CH_3)_3P-H]^+$, the present results also indicate that the proton cannot be undergoing rapid site exchange; i.e., any proton jumping must be at a rate much slower than 500 Hz. By contrast, studies of chemisorbed pyridine on H–Y have shown that the pyridinium ion is desorbed from a hydroxyl site as a pyridine molecule after a mean time of ∼5 × 10^{-7} s (40 C). The

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desorbed pyridine molecule jumps to another hydroxyl site to form a new pyridinium ion. On a less frequent time scale of $\tau \sim 10^{-5}$ s, the pyridinium ion jumps as an intact unit to another oxygen site in the zeolite framework.[33] Comparison of results suggests that the 3650-cm^{-1} hydroxyl proton in the present sample is complexed more tenaciously by trimethylphosphine. This may imply that $(CH_3)_3P$ behaves as a stronger base than pyridine under these conditions or that the Brønsted sites are more acidic in the present samples. More detailed comments are not warranted since pore-filling factors, etc., are likely to be very different between the two studies.

The rapid motion of a cation, such as $[(CH_3)_3P-H]^+$, in a dehydrated zeolite is not unreasonable. The classic example of cation motion in a dehydrated zeolite is that of the proton itself; indeed this motion is central to the concept of Brønsted acidity and dehydroxylation of zeolites.[30] From the results of Freude et al.,[30] one can calculate a proton jump rate of ~ 500 Hz at room temperature in the absence of an absorbate. As noted above, this jump rate can be substantially increased when a base such as pyridine and, by extension, trimethylphosphine is introduced.

The presence of intense, dipolar-derived spinning sidebands in the coupled spectrum of the 400°C-HY-80°C(0.5h) sample (Figure 3b) shows that the major species present here ("type II", δ_P -2.3) cannot be involved in rapid isotropic rotational jumps, in contrast to the behavior of the sample degassed at 300 °C. The observation of a large phosphorus-proton J coupling is also important since an increase in one-bond P-X couplings can be explained on the basis of increased s character in the P-X bond;[34] e.g., J increases from 182 Hz for PH_3 (p^3 hybridization) to 548 Hz for PH_4^+ (sp^3, hybridization). Therefore, the major species in the 400°C-HY-80°C(0.5h) sample must involve covalent bonding to a proton. We propose a complex of the type

B
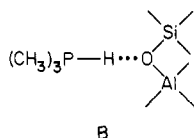
Since the J coupling is well resolved, any proton chemical exchange must be at a rate much slower than ~ 500 Hz. A relatively strong bond to a lattice oxygen is proposed to explain the absence of rapid motion. Since this complex is apparently thermally dissociated by desorption at 300 °C, it appears to be most likely derived from the 3550-cm^{-1} hydroxyl group and associated with weaker Brønsted sites. Previous work has also suggested that the 3550-cm^{-1} group corresponds to a weaker Brønsted site,[32] although there is conflicting evidence.[35]

It is tempting to interpret these results in terms of conventional dissociation constants for strong and weak acids. The zeolite lattice is the conjugate base. Proton donation to the base $((CH_3)_3P)$ may be complete in the case of the strong acid site or incomplete in the case of the weak acid site. Thus, the spectrum observed after degassing at 300 °C would be a better measure of strong acidity in zeolites.

We postulate that both the type II hydrogen-bonded complex and the type I mobile phosphonium ion (arising from the 3650-cm^{-1} hydroxyl group) are present in the sample degassed at 80 °C (Figure 3a and b). The inability to resolve the two components could arise from slow exchange between type I and type II complexes (no proton jumping) in analogy to the slow pyridinium *ion* exchange in H-Y (see above). Such an exchange could account for the monotonic change in chemical shift as the sample is degassed (Table I). Alternately, it is plausible that the type I complex is not formed until the sample is exposed to the higher desorption temperatures. However, this does not appear likely from an acid-strength point of view and is not suggested by the infrared data. We do not mean to imply from these results that

all the 3550-cm^{-1} hydroxyls and all the 3650-cm^{-1} hydroxyls are alike; i.e., there may be more than two different levels of acidity.

We hypothesize that the large line width in the coupled spectrum of the 100 °C desorbed sample, Figure 3d, may arise from interference between incoherent motion due to site exchange (type I $\leftrightarrow$ type II) and coherent averaging of the $^{31}P-^1H$ dipole–dipole coupling by magic-angle spinning.[36] From the calculated[8] P-H second moment for $[(CH_3)_3P-H]^+$, one can derive an estimate of ~ 5 kHz for the maximum broadening by using the approach of Rothwell and Waugh.[36]

Additional NMR Observations. Air exposure apparently results in the formation of oxidative byproducts. The most obvious reaction that could occur is the conversion of trimethylphosphine to the oxide $(CH_3)_3PO$. $(CH_3)_3PO$ in $CDCl_3$ produces a ^{31}P resonance at +38.4 ppm; solid $(CH_3)_3PO$ resonates at +41 ppm (this study). A weak resonance was observed at +38 ppm in one sample, but most of the "oxidative" resonances appear further downfield, typically in the range 50-70 ppm (common for trialkylphosphine oxides). However, trimethylphosphine oxide can itself form a variety of acid-base complexes, e.g., $(CH_3)_3PO-Al(CH_3)_3$,[37] $(CH_3)_3PO-BF_3$ (δ_P +69.2),[38] $(CH_3)_3PO-HOCOCH_3$ (δ_P +44.8),[39] and $(CH_3)_3PO-HOCOH$ (δ_P +46.0).[39] In addition, the ^{31}P chemical shifts of trialkylphosphine oxides are sensitive to hydrogen bonding. For example, Symons and Eaton[40] have measured ^{31}P shifts from $\sim +43$ to $\sim +66$ ppm for $(CH_3CH_2)_3PO$ in solvents ranging from hexane to water. Our own measurements have shown that the resonance of $(CH_3)_3PO$ changes from +38.4 ppm in $CDCl_3$ to +51 ppm in D_2O. Therefore, the species observed in the 50-70 ppm region can be ascribed here to trimethylphosphine oxide formation with subsequent chemisorption to acidic sites and/or hydrogen bond formation to zeolitic protons or adsorbed water. Reference to Figure 2d suggests that the Brønsted complex is more inert to these reactions.

Schoonheydt et al.[9] have sugggested that $(CH_3)_3P$ complexes with the zeolite framework oxygens. Although we cannot rule this out by NMR (its chemical shift could be in the 50-70 ppm range), based on peak areas in this region, it most likely constitutes a rather minor component in the present samples. The origin of the weak resonances $\sim +23$ and $\sim +26$ ppm is uncertain; they may be related to the unidentified "chemisorbed residues" noted by Schoonheydt et al.[9]

Relatively minor spectral changes were noted when the 400°-C-HY-80°C(1h) sample was exposed to H_2O vapor. We speculate that these effects are explained by weak hydrogen bonding to adsorbed H_2O and perhaps involve a shift between populations of type I and type II species.

$(CH_3)_3P$ as an NMR Probe. The above results demonstrate that trimethylphosphine is an effective probe molecule for studying acid sites in zeolites. In this regard, other trialkylphosphines having longer alkyl chains could be used to probe selectively sites on catalytic surfaces accessible only to larger molecules. Trimethylphosphine exhibits high sensitivity both for NMR and IR spectroscopy. Moreover, the NMR chemical shifts are sufficiently large that one can easily resolve differences between Brønsted acid sites and variety of Lewis sites; quantitative studies should be straightforward due to short ^{31}P T_1's. It would be desirable to establish a correlation between ^{31}P chemical shifts and surface acidity. However, the variability of factors influencing ^{31}P chemical shifts and the dominance of the paramagnetic term in determining ^{31}P chemical shifts suggest that this should not be attempted a priori.[34] Nevertheless, it is interesting to note the similarity in increased downfield chemical shift for the $AlCl_3$ complex relative to the $\gamma-Al_2O_3$ complex and the assignment of greater acidity to $AlCl_3$ from ESR studies by using di-*tert*-butyl nitroxide as a probe.[41] A firmer basis for correlating ^{31}P chemical

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shifts with surface Lewis acidity must await the results of additional thermal desorption studies.

Conclusions

We have demonstrated that trimethylphosphine is a useful NMR probe molecule for acid site characterization of zeolites and, most likely, of catalytic surfaces in general. When trimethylphosphine is adsorbed on a 400 °C calcined H–Y zeolite, both [(CH$_3$)$_3$P–H]$^+$ species and, depending on desorption conditions, physisorbed (CH$_3$)$_3$P are detected. Clear evidence for a phosphonium ion is found from well-resolved J_{P-H} coupling. Calcination of H–Y at 500 °C and above gives rise to a number of additional ^{31}P resonances that can be assigned to Lewis sites. These results support the concept of a heterogeneous Lewis site distribution in calcined H–Y zeolites. A resonance that can be ascribed to a (CH$_3$)$_3$P/Al$_2$O$_3$ complex is noted at 500 °C and above, providing independent evidence to support the previous findings of Freude et al.[22b] Poorly resolved coupling for another

species in the 500 °C calcined sample provides evidence for a site that coordinates (CH$_3$)$_3$P both to a proton and a Lewis acid. This type of site may be responsible for the strongly acidic properties of zeolites in heterogeneous catalysis.

Thermal desorption studies of the 400 °C calcined H–Y suggest that there are at least two [(CH$_3$)$_3$PH]$^+$ complexes: (1) a rather immobilized phosphonium complex with a chemical shift of -2.3 ppm that dominates the spectrum from the sample degassed at 80 °C for 0.5 h and (2) a mobile phosphonium ion with a chemical shift of -4.4 ppm which is observed for a sample degassed at 300 °C. The former complex appears to arise from interaction with 3550-cm^{-1} hydroxyl groups and the latter with 3650-cm^{-1} hydroxyl groups.

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Vibrational Circular Dichroism in Amino Acids and Peptides. 9. Carbon–Hydrogen Stretching Spectra of the Amino Acids and Selected Transition-Metal Complexes

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Abstract: Vibrational circular dichroism (VCD) spectra have been obtained in the carbon–hydrogen stretching region for lactic acid, 21 α-amino acids, 5 bis(amino acid)copper(II) complexes, and a tris(alaninato)cobalt(III) complex. The spectra of the amino acids, which include most of those that occur naturally, were obtained in D$_2$O without pD adjustment. A common feature of nearly all of these spectra is a positive VCD bias for the L-amino acids resulting from a broad band associated with the methine C$_\alpha$*H stretching mode located near 2970 cm^{-1} in the free amino acids. Evidence is presented that associates the strong positive methine VCD intensity with the presence of an intramolecular hydrogen bond between the ND$_3^+$ and CO$_2^-$ groups in the amino acids. Further intensification of this VCD band in the bis-copper (II) complexes is attributed to increased bonding strength between the amine and carboxylic acid groups via the transition-metal bonds. The mechanism of positive VCD intensity enhancement is proposed to arise from a current in a ring that is closed by the intramolecular hydrogen bond or the transition-metal bonds. The remaining VCD features are associated with the CH stretching modes of the side chains of the amino acids.

I. Introduction

The solution-state conformation of amino acids is of considerable interest owing to the role that these molecules play in the determination of the structure and function of small peptides and proteins. The conformation of an amino acid involves the geometry of the amine and carboxylic acid groups on the one hand and that of the side-chain group on the other. The problem of specifying the various torsional angles describing the conformational degrees of freedom for amino acids in solution is formidable, although significant progress has been achieved in recent years by using NMR spectroscopy.[1] Vibrational spectroscopy has contributed qualitatively to the problem; however, neither infrared nor Raman spectroscopy has yet been used for quantitative determination of amino acid conformations.[2]

A new approach to the determination of conformational details in chiral molecules known as vibrational circular dichroism (VCD) has been developed recently.[3] In previous publications we have reported VCD spectra in the CH stretching region for alanine, simple alanyl peptides, and serine.[4] The combination of the infrared absorption spectrum and the VCD spectrum, where the

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