

# Reaction of the Hydroxy Groups of Zeolites with Phosphorylating Agents

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**ABSTRACT:** *Hydroxy groups on the surface of zeolite Y can be converted to phosphate groups by reaction with alkyl phosphoric acids as well as with metaphosphates when generated in the presence of the solid. Phosphonic and phosphinic acids also reacted readily with the OH groups. The products were characterized by  $^{31}\text{P}$ ,  $^{29}\text{Si}$ , and  $^{27}\text{Al}$  NMR spectroscopy. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 691–698, 1998*

## INTRODUCTION

Previous work in our laboratory [1] has shown that it is possible to attach phosphoryl functions of various types directly to the surface of silica gel by reacting the OH groups on the surface with the powerfully electrophilic alkyl metaphosphates ( $\text{RO-PO}_2$ ). This species was generated by thermal fragmentation of derivatives of the 2,3-oxaphosphabicyclo[2.2.2]octene ring system [2a] (e.g., 1) or of *O*-alkyl *N*-substituted phosphoramidic acids [3] (e.g., 2) as seen in Scheme 1. It was also found that phosphorylation of the surface could be effected simply by direct reaction of the OH groups with readily available phosphorus acids (alkyl phosphoric, phos-

phonic and phosphinic acids) [4]. We now have applied our phosphorylation procedures to zeolites, and describe our results in this article.

Hydroxy groups are found in various forms in zeolites. They constitute a bridge between silicon and aluminum in the aluminosilicate framework, where they occur in the strongly acidic structural unit  $\text{Si-O(H)-Al}$  [5]. They are present as terminal silanol groups ( $\text{Si-OH}$ ) at sites where dealumination has occurred in the process of preparing the zeolite, as well as by migration of silicon atoms at the surface of mesopores [6]. They are also found on extra-framework alumina [7], which in part may be in the form  $\text{Al(OH)}_3$  or  $\text{Al(OH)}^{2+}$ . That the bridging and silanol groups are accessible to electrophilic agents has been demonstrated by their reactivity to silylating agents, which accomplished the attachment of siloxy substituents to the solid as determined by effects on OH stretching signals of the infrared spectrum [5c]. It is reasonable therefore to expect that phosphorylation could occur at these types of OH on the zeolite framework.

The concept of modifying zeolites with phosphorus chemicals is not new, and some valuable changes in catalytic activity have resulted from various treatments of the solids. Reports are scattered in the literature on methods for incorporating phosphorus and on the nature of the modified zeolite. In general, however, there is little direct structural information on the nature of covalent attachments of the phosphorus groups to the zeolite. An early example of a reaction with a phosphorus compound made use of trimethyl phosphite [8], which is believed [8–10] to undergo transesterification with an OH on the sur-

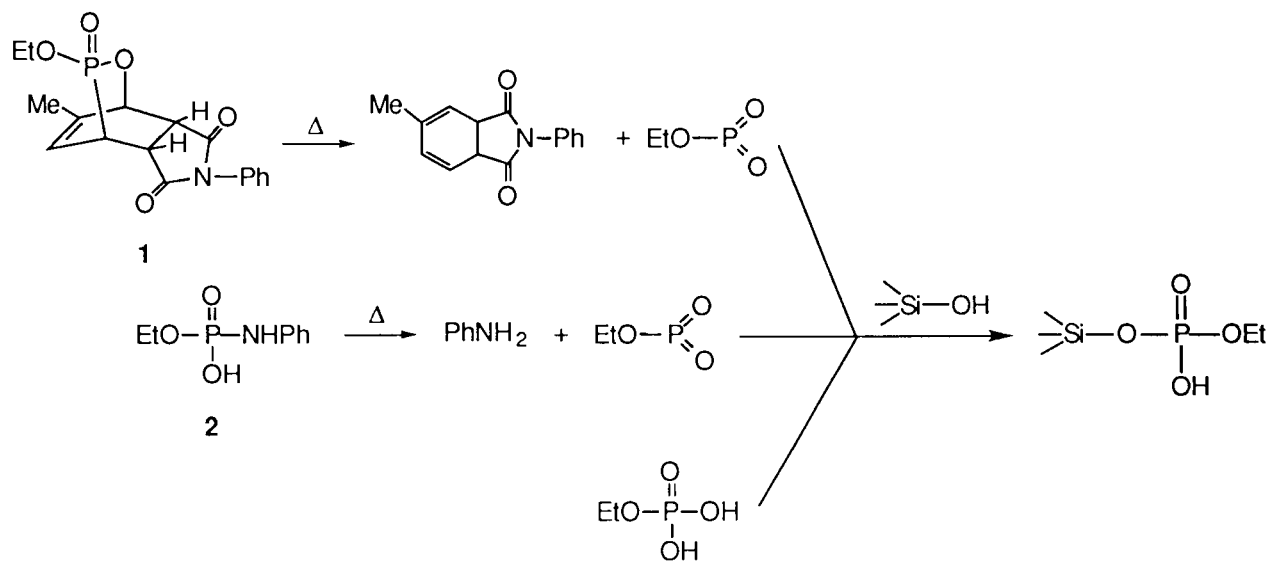
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Dedicated to our distinguished colleague Professor Robert R. Holmes on the occasion of his retirement from the University of Massachusetts.

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SCHEME 1

face (Z) to form Z-OP(OMe)<sub>2</sub>, ultimately converted to Z-OP(O)(OH)<sub>2</sub>. Neither grouping has been confirmed by NMR spectroscopy, however. Phosphorus pentachloride also reacts with the OH groups [11], presumably giving structures such as Z-OPCl<sub>4</sub> as suggested by <sup>31</sup>P NMR ( $\delta = 18.2$  and  $\delta = 22.4$ ); much dealumination occurred in this reaction, with introduction of PO<sub>4</sub><sup>3-</sup> into the framework (<sup>31</sup>P NMR  $\delta = 30$ ). Trimethylphosphine appears to be protonated by the acid sites [12] and is attached as the ion Me<sub>3</sub>PH<sup>+</sup>. Phosphoric acid causes extensive dealumination [12], but a recent report [13] on the treatment of ZSM-5 suggests that the group OP(O)(OH)<sub>2</sub> can become attached to the surface if the ZSM-5 is synthesized in the presence of phosphoric acid. This was indicated by a <sup>31</sup>P NMR shift of  $\delta = 2.5$ . There was a reduction in the catalytic activity that was consistent with the removal of some of the strongly acidic Brønsted sites, an observation also made in earlier studies with phosphoric acid as well as with trimethyl phosphite and trimethylphosphine [12,14]. Other phosphorus reagents that have been used include [15] Ph<sub>2</sub>PCl and Ph<sub>2</sub>P(O)H (shown [15] in the tautomeric form Ph<sub>2</sub>P-OH). The nature of the bonding to the zeolite was not characterized, but for the former, it is likely that attack on OH groups has occurred.

In exploring the application of our phosphorylating systems to zeolites, we have examined the behavior of four representative materials, but with greater attention paid to the case of zeolite Y, which on analysis by solid-state NMR techniques gave rea-

sonably compact resonances. The simplest phosphorylation procedure is that consisting of heating the solid with a phosphorus acid in an inert solvent; in addition to this procedure, we have performed phosphorylations by generating alkyl metaphosphates, by the methods shown in Scheme 1 using precursors 1 and 2, in the presence of the solid. As will be seen, all procedures gave the same product as confirmed by solid-state <sup>31</sup>P and <sup>29</sup>Si NMR. <sup>27</sup>Al NMR was also performed in some cases to probe the possibility that structural changes, such as a significant degree of dealumination, might be revealed.

## EXPERIMENTAL

### Phosphorus Compounds

The bicyclic phosphonate 1 was available from previous work [2], as was the phosphoramidic acid 2 [3]. Monoalkyl phosphoric acids were prepared by conventional methods; phosphonic and phosphinic acids were commercially available.

### Zeolites

The zeolites were obtained from commercial sources and were received in the H<sup>+</sup> form. Immediately before use, they were dried in an oven at 350°C for 2 hours with nitrogen flushing. Surface water destroys the metaphosphates when these are used for phosphorylation; the direct reaction of phosphorus acids is less sensitive to trace amounts of water.

### Direct Phosphorylation by Phosphorus Acids

A mixture of 0.25 g of the dry phosphorus acid and 1 g of the zeolite was refluxed in 20 mL of toluene; acetonitrile could also be used. The reaction was conducted in a Soxhlet apparatus with anhydrous sodium sulfate in the thimble to remove water as formed in the reaction. The product was washed and analyzed in the manner already described.

In one case (PhHP(O)OH), the reaction was conducted at room temperature in acetonitrile, giving a product with the same  $^{31}\text{P}$  NMR signal ( $\delta$  11.2) as found for the product from refluxing toluene.

### Phosphorylation with Metaphosphates

The bicyclic phosphonate **1** as the precursor was dissolved in toluene (freshly dried over sodium and distilled), or chlorobenzene (freshly distilled under nitrogen), and the dry zeolite was suspended in the solution. The same arbitrary amount of reactant was used for all of the zeolites (0.60 mmol per gram of zeolite). The mixture was refluxed for 3–4 hours under nitrogen or argon, and then cooled and filtered. The solid was washed with toluene to remove the dihydrophthalimide coproduct, and with isopropyl alcohol and finally  $\text{CH}_2\text{Cl}_2$  to remove any adsorbed phosphate that might be present as a result of a water-metaphosphate reaction. The product was dried in a vacuum desiccator and examined spectroscopically (see later discussion). Phosphorus content was determined on a few samples as described elsewhere [4].

With phosphoramidic acid **2** as the metaphosphate generator, the reactant ratio was 1.0 mmol per gram of zeolite. Reactions were conducted in toluene solution at reflux; only 1–2 hours were required to achieve fragmentation to the metaphosphate. The product was washed and dried as already described and treated in the same way.

### Spectroscopic Methods

Solid-state NMR spectra were obtained at 200 or 300 MHz using a Bruker AC200 with IBM solids rack or a Bruker ASX300, respectively. In all cases, the pulse power for each nucleus was adjusted to be a  $5\ \mu\text{s}$   $90^\circ$  pulse (50 kHz spin lock field). When a shorter pulse of  $0.5\ \mu\text{s}$  was used, no changes were observed in the shape of the  $^{27}\text{Al}$  NMR signals. Other pertinent parameters are given in Table 1. All phosphorylated zeolites were examined by  $^{31}\text{P}$  NMR using the cross-polarization magic angle spinning (CP-MAS) technique. Zeolite Y and its product from *O*-ethyl phosphorylation were also examined by  $^{29}\text{Si}$  and  $^{27}\text{Al}$

NMR.  $^{29}\text{Si}$  spectra without cross-polarization and proton decoupling were run with 15 s intervals. An increase in the intervals between pulse sequences did not produce any change in the spectra. The spectral data obtained are given in Tables 2–5 and some representative spectra are shown as Figures 1–3.

## RESULTS AND DISCUSSION

Most of the work on characterizing the product of reaction of zeolites with the various phosphorylating systems was performed on a zeolite Y with a nominal Si:Al value of 5. This work is described in detail first, followed by brief discussion of results with other zeolites.

### Characterization of the Zeolite Y by $^{29}\text{Si}$ and $^{27}\text{Al}$ NMR

The  $^{29}\text{Si}$  MAS NMR spectrum of the starting zeolite Y (Figure 1a) sample showed four absorption signals:  $\delta - 93$  (for  $n = 3$ , where  $n$  is the number of attached Al groups),  $\delta - 98$  ( $n = 2$ ),  $\delta - 103$  ( $n = 1$ ) and  $\delta - 108$  ( $n = 0$ ). A signal for  $n = 4$  should occur around  $\delta - 85$  but is frequently absent when Si:Al  $> 2$  [16]. When the spectrum was run with cross-polarization from  $^1\text{H}$ , only the signal at  $\delta - 103$  was enhanced (Figure 1b). This signal therefore is a composite of that from  $(\text{SiO})_3\text{Si-O-Al}$  and that from  $(\text{SiO})_3\text{Si-OH}$ , in agreement with the literature [17]. The spectra were deconvoluted in terms of gaussian peak shapes and the areas of the individual deconvoluted peaks were used to calculate the ratio of tetrahedral Si and Al in the zeolite framework from the formula

$$\text{Si/Al} = \frac{\sum I_{\text{Si}(n\text{Al})}}{\sum (n/4)I_{\text{Si}(n\text{Al})}}$$

where  $I_{\text{Si}(n\text{Al})}$  is the intensity of the signal for  $n$  Al atoms. The relative intensities of the signals are given in Table 3. The ratio was found to be 4.9. However, because the signal at  $\delta - 103$  also contains a contribution from a Si-OH group, the real ratio is probably slightly higher than that calculated.

Framework (tetrahedral) Al in zeolites gives a  $^{27}\text{Al}$  NMR signal at  $\delta + 50$  to  $+ 80$  [18a]. Nonframework Al [18b] gives a very broad signal, seen as a rise in the baseline. A relatively sharp signal also occurs at  $\delta 0.35$ – $3.5$ . The former is ascribed to “polymeric alumina,” the latter to octahedral species such as  $\text{Al}(\text{OH})_6^{3+}$ . In accordance with these generalities, the specimen of zeolite Y studied here gave signals at  $\delta + 59$  for framework Al, and at  $\delta - 2$  for the nonfra-

**TABLE 1** Parameters of NMR Experiments

Instrument MHz	Nuclei	Experiment	Repetition time, s	Contact time, ms	Spin kHz	No. scans	External reference
300	<sup>27</sup> Al	D <sup>a</sup>	0.5	—	8.0	64	AlCl <sub>3</sub> <sup>c</sup>
200	<sup>29</sup> Si	CP <sup>b</sup>	5	10	3.5	500–1000	DSS <sup>d</sup>
200	<sup>29</sup> Si	D <sup>a</sup>	15	—	3.5	2500–4000	DSS <sup>d</sup>
200	<sup>31</sup> P	CP <sup>b</sup>	5	1.5	4.5	500–1000	CaHPO <sub>4</sub>

<sup>a</sup>Direct Bloch decay with proton decoupling.<sup>b</sup>Cross-polarized.<sup>c</sup>1 M water solution.<sup>d</sup>Sodium 2,2-dimethyl-2-silapentane-5-sulfonate.**TABLE 2** <sup>31</sup>P NMR Shifts and P Content of Phosphorylated Zeolite YH

Sample <sup>a</sup>	<sup>31</sup> P NMR, $\delta$	% P
1	–14.2	0.65
2	–11.4	1.24
3	–12.6; –17.8	1.71
4	–15	1.75
5	14.9	3.62
6	6.0; 2.6	3.03

<sup>a</sup>From phosphorylation with: (1) reagent 1; (2) reagent 2; (3) EtOPO(OH)<sub>2</sub>; (4) (–)Menthyl-O-PO(OH)<sub>2</sub>; (5) MePO(OH)<sub>2</sub>; (6) PhPO(OH)<sub>2</sub>.

mework Al formed by dealumination in the procedure used to synthesize the zeolite [18] (Figure 3a).

These <sup>29</sup>Si and <sup>27</sup>Al NMR spectral properties of the parent zeolite will be seen to provide a useful aid in understanding the chemical changes occurring on phosphorylation, for indeed some significant changes in the spectra are observed after the reactions.

### Reaction of Zeolite Y with Alkyl Phosphates

Refluxing a suspension of zeolite Y in toluene containing ethyl phosphate (EtO-PO(OH)<sub>2</sub>) in an arbitrary weight ratio of 4:1, respectively, gave a solid product that after drying was found to contain 1.71% P on analysis. No other reactant ratios have yet been studied. That the phosphorus was covalently bonded to the surface, and not just present as adsorbed ethyl phosphate, was clearly seen from the <sup>31</sup>P NMR signal (Figure 2a), which occurred at  $\delta$  – 12.6, with a smaller signal at  $\delta$  – 17.8. The upfield shifting to  $\delta$  – 12.6 from the value of the starting acid ( $\delta$  0.4 [4]) is the result of replacement of H on P-OH by a heavy atom such as Si, an effect well established from studies of phosphorylated silica gel. Adsorbed ethyl phosphate gave a signal at  $\delta$  0. The small signal at  $\delta$  – 17.8 could arise from a pyrophosphate moiety attached to the surface.

**TABLE 3** The Relative Intensities<sup>a</sup> of <sup>29</sup>Si NMR Signals for Zeolite YH Before and After Phosphorylation

Sample <i>b</i>	Si( <i>n</i> Al)				Si/Al
	<i>n</i> = 3 $\delta$ – 93	<i>n</i> = 2 –98	<i>n</i> = 1 –103	<i>n</i> = 0 –108	
— <sup>c</sup>	6.7	17.2	26.8	49.3	4.9
1	11.7	12.0	36.5	39.8	4.2
2	10.3	11.7	37.4	40.7	4.4
3	10.7	11.1	34.0	44.2	4.5
4	4.1	18.3	33.8	43.8	4.8
5	5.1	12.6	28.4	53.9	4.1
6	16.1	8.7	32.3	42.8	4.1

<sup>a</sup>From peak areas.<sup>b</sup>Defined in Table 2.<sup>c</sup>Untreated zeolite Y.**TABLE 4** <sup>27</sup>Al NMR Shifts of Untreated and Phosphorylated Zeolite YH

Sample <sup>a</sup>	Tetrahedral	Octahedral
—	+59	–2
1	+60	–1
2	+59	–3
3	+58	–2, –17
4	+58	–2, –14
5	+57	–14
6	+55	–4, –22

<sup>a</sup>Defined in Table 2.

In the <sup>29</sup>Si CP-MAS NMR spectrum (Figure 1c), the major change was a small but important reduction in the intensity of the signals at  $\delta$  – 103 composed of Si(1Al) and SiOH (cf. Figure 1b to 1c). This is the result of the removal by phosphorylation of the hydroxy hydrogen and loss of the signal enhancement caused by it. As in the case of silica gel, no new signal for phosphorylated silicon could be discerned. Using the intensities given in Table 3, the ratio of Si to Al in the framework was calculated to be 4.5. This value is close to that found for the starting zeolite

TABLE 5  $^{31}\text{P}$  NMR Spectral Data for Alkyl Phosphorylated Solids<sup>a</sup>

Zeolite	Phosphorylating Agent				
	Ethyl Metaphosphate		EtOPO <sub>3</sub> H <sub>2</sub>	MenOPO <sub>3</sub> H <sub>2</sub> <sup>b</sup>	BuOPO <sub>3</sub> H <sub>2</sub> <sup>c</sup>
	from 1	from 2			
Mordenite <sup>d</sup>	-11 (0.48)	-10	-10	-12	-10
Mordenite <sup>e</sup>	-9 (0.49)	-10			
ZSM-5	-12 (0.52)	-8	-6	-12	-7
Silica gel	-9.9 <sup>f</sup>	-10 <sup>g</sup>	-10 <sup>h</sup>		

<sup>a</sup>Bands typically were 30–50 ppm at the baseline, and the maximum was also broad and ill-defined. Values following the shifts in parentheses are % P.

<sup>b</sup>(-)-Menthyl-O-PO<sub>3</sub>H<sub>2</sub>.

<sup>c</sup>(+)-sec.-ButylO-PO<sub>3</sub>H<sub>2</sub>.

<sup>d</sup>Si:Al = 18.

<sup>e</sup>Si:Al = 48.

<sup>f</sup>Ref. 2b.

<sup>g</sup>Ref. 3.

<sup>h</sup>Ref. 4.

(4.9), bearing in mind the inaccuracy of this value due to the fact that this signal is a composite containing a contribution from a Si-OH moiety. That the two values do match reasonably closely is taken to mean that little or no dealumination of the zeolite framework has occurred during the phosphorylation. This point was then confirmed by the  $^{27}\text{Al}$  NMR spectrum (Figure 3c); the tetrahedral framework Al signal at  $\delta + 58$  remained the same in relative peak area. A new signal of about 20% of total area appeared at  $\delta 17$ , which we attribute to octahedral Al where a phosphate group has been coordinated. This signal might arise from action of the phosphoric acid on extra-framework polymeric Al<sub>2</sub>O<sub>3</sub>. We have found a similar signal ( $\delta - 19$ ) developing in alumina after phosphorylation by a mixture of P<sub>2</sub>O<sub>5</sub> and isopropyl alcohol (yielding mono- and di-isopropyl phosphates). Also, similarly upfield signals have been reported [5a] in aluminophosphate molecular sieves and in silicoaluminophosphates [5d]. Here as in zeolites, tetrahedral Al gave signals around  $\delta 30$  to 45; the additional upfield signals at  $\delta - 10$  to  $-19$  were ascribed to octahedral Al coordinated to a phosphate.  $^{31}\text{P}$  NMR signals for these samples appeared at  $\delta - 23$  to  $-31$ . The small  $^{31}\text{P}$  signal we observed in phosphorylated zeolite Y at  $\delta - 17.8$  possibly could be associated with the Al species giving the upfield  $^{27}\text{Al}$  signal at  $\delta - 18$ , but as noted the assignment of this signal to a pyrophosphate structural feature may be more reasonable.

(-)-Menthyl phosphate was also used for phosphorylation of zeolite Y. The product had  $^{31}\text{P}$  NMR  $\delta - 15$ , and similar  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR spectra (Tables 3 and 4) to the ethyl phosphate product. It is thus seen that it is quite feasible to react more complicated phosphates with the surface.

### Phosphorylation of Zeolite Y by Ethyl Metaphosphate

The two reagents 1 and 2 used in our previous work for ethyl metaphosphate generation were thermally fragmented in the presence of zeolite Y. The P content of the two samples (0.65 and 1.24%, respectively) was somewhat lower than that from the use of ethyl phosphate (1.71%), but both gave strong  $^{31}\text{P}$  NMR signals (from 1, Fig. 2b). The shifts ( $\delta - 14.2$  and  $-11.4$ , respectively) match that from the use of ethyl phosphate ( $\delta - 12.6$ ). No additional upfield pyrophosphate signal as found in the latter was present. The  $^{29}\text{Si}$  spectra (Table 3) were practically identical to those from the ethyl phosphate reaction, and we conclude that the site of phosphorylation on the framework is similar in all three samples. It is especially significant that the use of neutral reagent 1 gave the same results as from the use of the acidic ethyl phosphate. No dealumination is likely with the neutral compound, and indeed the Si:Al values for the three samples from the different phosphorylation procedures were all similar, in the range 4.2–4.5 (Table 3).

A significant difference was noted in the  $^{27}\text{Al}$  NMR spectra of these products: the expected signals for tetrahedral and octahedral Al were observed (Table 4), in the same relative intensity, but the third signal at  $\delta - 18$ , observed after the ethyl phosphate reaction, was missing (Figure 3b). This implies that the octahedral moiety giving the signal at  $\delta - 18$  is not formed by reaction with framework Al but is the result of a second reaction with nonframework Al. Because the powerfully electrophilic ethyl metaphosphate does not give this moiety, it must be concluded that attack on Al-OH is not involved. The P

content of the zeolite reacted with ethyl phosphate (1.71%) also was much higher than that from use of ethyl metaphosphate, suggesting a reactive capability for ethyl phosphate (e.g., as a ligand) that is missing in the metaphosphate.

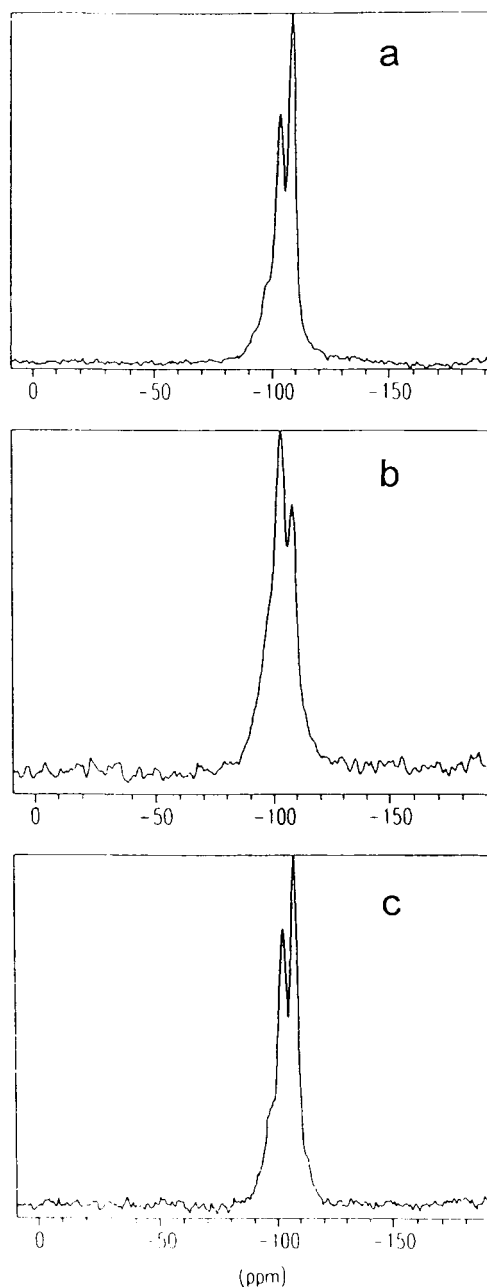
#### Reaction of Zeolite Y with Other Phosphorus Acids

Two phosphonic acids (methyl and phenyl, giving products 5 and 6, respectively) were employed successfully in the direct reaction with zeolite Y. The P content of these products (5, 3.62%, 6, 3.03%) was much higher than that of the ethyl phosphate product (1.71%). In each case, the  $^{31}\text{P}$  NMR shifts [5,  $\delta$  14.9 (Figure 2c); 6, 6.0] appeared significantly upfield from the starting acids ( $\delta$  25.7 and 14.5, respectively), just as seen for the use of alkyl phosphates. The  $^{29}\text{Si}$  spectra (Table 3) resembled those from the use of the phosphates, and Si:Al values of the same magnitude were observed, again taken to mean that dealumination was not significant. The  $^{27}\text{Al}$  NMR spectra also were similar to those from the phosphates, showing not only the expected tetrahedral and octahedral Al signals but also an additional upfield signal (5,  $\delta$  - 14; 6,  $\delta$  - 22, Figure 3d) of about 20% of the total area as seen when ethyl phosphate was used. It appears to be a general property, then, for phosphorus acids to react not only with framework OH groups but also with extra-framework Al.

Two phosphinic acids ( $\text{Ph}_2\text{P}(\text{O})\text{OH}$  and  $\text{PhHP}(\text{O})\text{OH}$ ) also reacted directly with the zeolite. The products have only been characterized by  $^{31}\text{P}$  NMR at this time, but gave signals in the expected positions ( $\delta$  11.5 and 11.2, respectively).

#### Phosphorylation of Other Zeolites

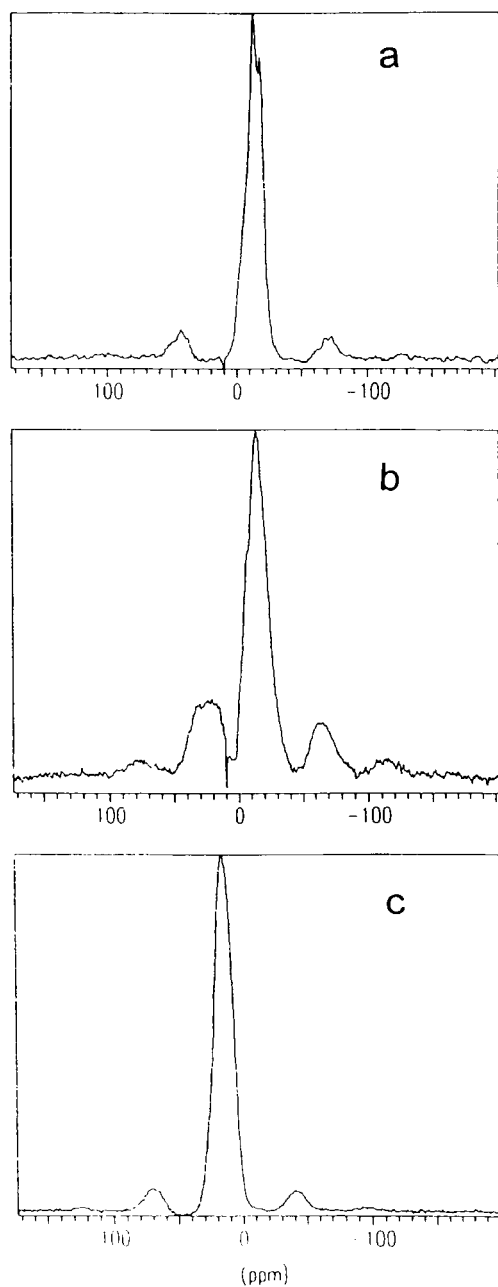
In Table 2 are  $^{31}\text{P}$  NMR shift data for three other zeolite samples that were subjected to phosphorylation with ethyl phosphate and with ethyl metaphosphate. In general, the signals occurred in the same upfield region as found for similarly treated zeolite Y. The samples phosphorylated by the metaphosphate released on thermolysis of the bicyclic phosphonate 1 were analyzed for phosphorus, giving values in the range 0.48–1.10% (Table 2). In addition, samples of ZSM-5 and mordenite were reacted directly with the optically active (-)-menthyl and (+)-*sec*.butyl phosphate, again giving products with the expected  $^{31}\text{P}$  NMR signals. We conclude that the various phosphorylation techniques are applicable in general to materials having the zeolite type of framework.



**FIGURE 1**  $^{29}\text{Si}$  NMR Spectra a: Zeolite Y; b: Zeolite Y with  $^1\text{H}$  cross-polarization; c: Zeolite Y after reaction with  $\text{EtOPO}(\text{OH})_2$ .

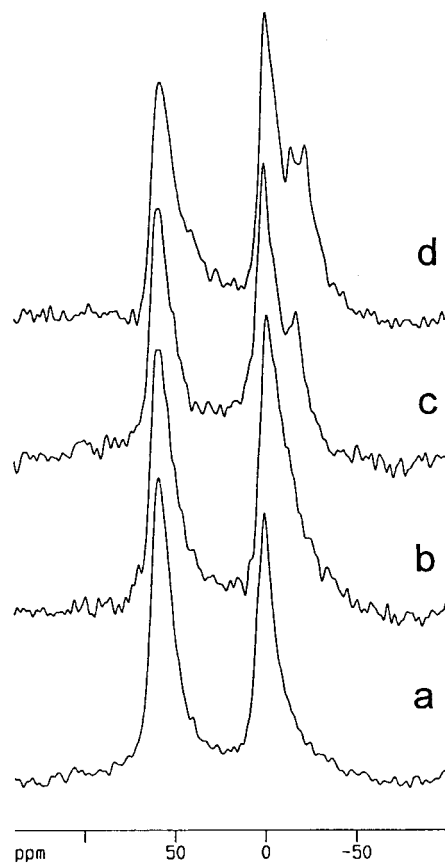
#### CONCLUSIONS

The various spectral data support the view that phosphorus functions have been attached covalently to zeolites by the direct reaction with phosphorus acids. The process is inexpensive and simple to carry out, but it remains to be seen if any special catalytic advantages are created in the modified zeolites.



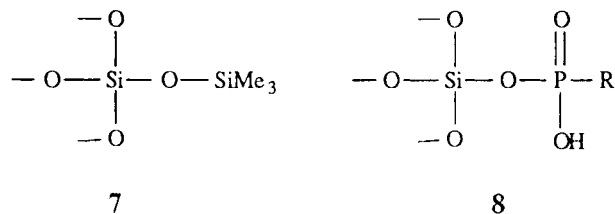
**FIGURE 2**  $^{31}\text{P}$  NMR Spectra. Zeolite Y after reaction with (a)  $\text{EtOPO}(\text{OH})_2$ , (b)  $\text{EtOPO}_2$  generated from reagent 1; (c)  $\text{MePO}(\text{OH})_2$ .

The structural feature created on the zeolite framework cannot be precisely specified at this time. In a study of the silylation of ZSM-5, it was shown that reaction could occur on both the terminal Si-OH groups as well as the bridging OH groups [5c]. Attack on the former would resemble the attack on the OH groups of silica gel, forming a siloxane linkage as in 7. Phosphorylation of a silanol group would

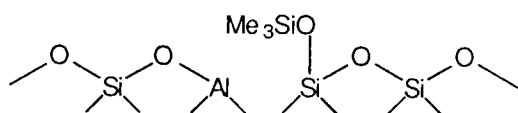


**FIGURE 3**  $^{27}\text{Al}$  NMR Spectra. (a) Zeolite Y (b) Zeolite Y after reaction with  $\text{EtOPO}_2$  from reagent 2 (c) Zeolite Y after reaction with  $\text{EtOPO}(\text{OH})_2$  (d) Zeolite Y after reaction with  $\text{PhPO}(\text{OH})_2$

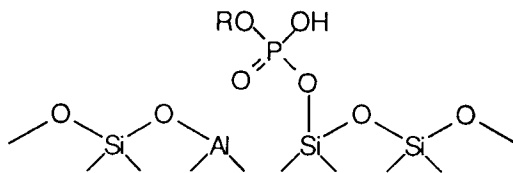
give rise to the related structural feature 8. However, it is possible that some of the phosphorus is in the form of a pyrophosphate with P-O-P links; the  $^{31}\text{P}$  NMR signals are quite broad, some covering as much as 30–50 ppm at the base, and the upfield end could rest in the pyrophosphate region. In one case (zeolite Y with ethyl phosphate), a discrete signal was observed in the pyrophosphate region.



Attack of the silylating agent on ZSM-5 [5c] was also proposed to take place on the bridging OH groups, resulting in creation of a siloxane group as in 9, where the bridge to Al is broken. This would gener-



9



10

## STRUCTURE

ate a free Lewis acid site on the Al of the framework. A similar feature (10) might be created in the phosphorylation reactions, but here it is probably that the Lewis acid site would interact with an oxygen of the phosphate group to create a new type of bridging unit. No  $^{27}\text{Al}$  NMR signal attributable to 3-coordinate Al was observed.

A recent article [19] has commented on the potential value of creating chirality in zeolites, as this modification might make it possible to use the materials as catalysts for asymmetric synthesis. Our phosphorylation chemistry offers one approach to supplying zeolites with sites of chirality, present in the form of groups attached directly to the silicon-aluminum framework. It was to demonstrate this feature of our methods that we included two phosphates with optically active alkyl groups ((-)-menthyl and (+)-*sec.*-butyl) in the P-alkoxy substituent. These phosphates are easily made and readily attached to the surface by heating the alkyl phosphate directly with the zeolite. It will be of interest to determine whether their presence will influence the stereochemical outcome of reactions occurring on the surface.

## ACKNOWLEDGMENTS

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