

## Measuring Brønsted Acid Densities in Zeolite HY with Diphosphine Molecules and Solid State NMR Spectroscopy

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In principle, the design and synthesis of new tailor-made catalysts, optimized for specific reactions, requires an ability to control distances between catalytic sites and an understanding of the activity and interactions between the catalytic sites. Along with the design of such materials comes the necessity to develop new characterization methods to probe these sites. This is particularly true for bifunctional catalysts (e.g., Pd/HZSM-5 catalysts for the hydrogenation of aromatics<sup>1</sup>), where the presence of two different, nearby active sites is required for reaction. Here we show results for new NMR probe molecules that can be used to estimate distances between catalytic sites. We have chosen to focus initially on molecules designed to probe acidity because of the widespread use of acid catalysts in a large range of applications<sup>2</sup> and recent efforts to synthesize Lewis acid catalysts in a controlled fashion.<sup>3</sup> In addition, the role that synergy between nearby acidic sites plays in controlling the strength of the acid sites remains controversial. Methods for quantifying the number of sites in close proximity to each other could prove useful in investigations of this phenomenon.<sup>4,5</sup>

Many techniques, including IR, temperature-programmed desorption, microcalorimetry, and solid-state NMR, combined with the sorption of basic probe molecules, have been applied to characterize acidity.<sup>6</sup> To date, only probe molecules with a single basic group have been used.<sup>6–12</sup> Here we report the use of a new class of probe molecules, diphosphines, which have two basic sites. These molecules can be employed, with <sup>31</sup>P NMR, to probe both the acidities and distances between acid sites in zeolites and on catalytic surfaces.

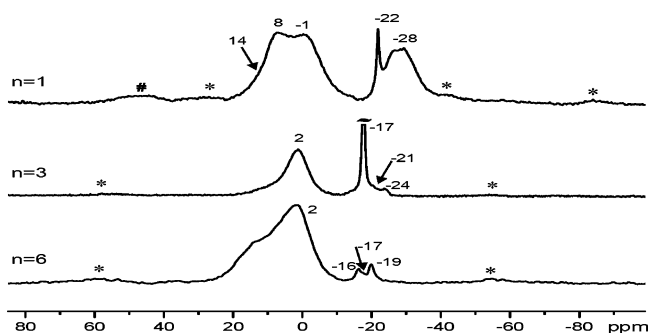
Diphenyldiphosphines, Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>, with *n* = 1, 3, and 6, were chosen as initial test probes, despite their sizes, because their monophosphine analogues are less mobile than smaller molecules such as trimethylphosphine, TMP. The distances between the two P atoms in these phosphines (from the literature or estimated on the basis of similar compounds) are 2.97,<sup>13</sup> 5.6,<sup>14</sup> and 9.4 Å<sup>15</sup> for the *n* = 1, 3, and 6 compounds, respectively. Acidities of these diphosphines in water were measured by potentiometric titration (Table 1).<sup>16</sup> The singly protonated *n* = 3 and 6 diphosphines are similar in acidic strength to protonated TMP (TMP is often used in <sup>31</sup>P NMR studies of acidity<sup>9–12</sup> and is a relatively strong Lewis base; p*K*<sub>a</sub> = 5.3 in H<sub>2</sub>O<sup>17</sup>), while their doubly protonated forms are much stronger acids, whose acidities are coincidentally similar to that of the singly protonated *n* = 1 diphosphine. Thus, these diphosphine molecules can probe a wide range of acidity because of their two active sites, diphosphines with smaller *n* (*n* < 3) probing even stronger acids. The basicities of the *n* = 3 and 6 diphosphines are similar, and thus, these molecules probe the distances between acid sites that are sufficiently acidic to protonate the phosphines or, in the case of Lewis acid site, that are bound directly to the phosphorus atom.

The <sup>31</sup>P MAS NMR spectra of zeolite HY (Si/Al ratio 2.6; approximately 47 Brønsted acid sites/unit cell) loaded with Ph<sub>2</sub>P-

**Table 1.** Acidities of the Protonated Diphosphines

	p <i>K</i> <sub>a1</sub> (expt <sup>a</sup> )	p <i>K</i> <sub>a2</sub> or p <i>K</i> <sub>a</sub> (expt)	p <i>K</i> <sub>a2</sub> or p <i>K</i> <sub>a</sub> (calcd)
PPh <sub>3</sub>	—	2.73	3.04
Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub>		2.46	
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub>	2.68	4.73	
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> PPh <sub>2</sub>	2.95	4.99	4.99

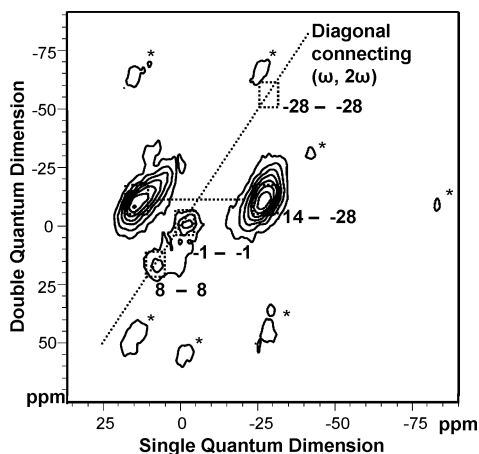
<sup>a</sup> See Supporting Information for details.



**Figure 1.** <sup>31</sup>P, <sup>1</sup>H decoupled, MAS NMR spectra of Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> sorbed on HY. Loading level = 12 molecules/unit cell. Spinning speed = 8 kHz. \* = spinning sideband, # = overlapping spinning sideband and diphosphine oxide impurity.

(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> (*n* = 1, 3, and 6) contain sharp, weak resonances due to the physisorbed, nonprotonated, mobile phosphine molecules at around -22, (*n* = 1), -17 and -24 (*n* = 3), and -16 and -19 ppm (*n* = 6) (Figure 1). Broader resonances are seen at similar frequencies (-28, -21, and -17 ppm, respectively), which are assigned to nonprotonated phosphorus atoms in either singly protonated or nonprotonated but more strongly physisorbed diphosphines. The broader, more intense resonances at -1, 8, and 14 ppm (shoulder) for *n* = 1 and 2 ppm for both *n* = 3 and *n* = 6 were enhanced in the <sup>1</sup>H-<sup>31</sup>P cross-polarization (CP) MAS experiments (Figure S1), consistent with their assignment to protonated phosphorus atoms.<sup>9,12</sup> These resonances can, in principle, result from either singly or doubly protonated phosphines, or both. For *n* = 3 and 6, the resonances must be due to the doubly protonated phosphines, because the intensity of the nonprotonated phosphorus resonances is close to negligible. For *n* = 1, both di- and monoprotinated phosphines must be present.

<sup>31</sup>P two-dimensional (2D) double quantum (DQ) NMR experiments were applied to probe P-P internuclear distances and confirm the spectral assignments. <sup>31</sup>P homonuclear dipolar couplings, and thus P-P distances, can be reintroduced in MAS experiments by using pulse sequences such as post-C7.<sup>18</sup> In the 2D versions of these experiments, two types of cross-peaks are observed; for two nearby sites with frequencies  $\omega_j$  and  $\omega_k$ , off diagonal peaks at  $(\omega_j, \omega_j + \omega_k)$  and  $(\omega_k, \omega_j + \omega_k)$  are seen, while for two sites with the same chemical shift,  $\omega_j = \omega_k = \omega$ , a single peak  $(\omega, 2\omega)$  on the single quantum (SQ)-DQ diagonal is observed. The <sup>31</sup>P 2D DQ



**Figure 2.**  $^{31}\text{P}$ ,  $^1\text{H}$  decoupled, 2D DQ NMR spectra of the  $n = 1$  sample (loading level = 8 molecules/unit cell).  $^1\text{H}$ – $^{31}\text{P}$  CP was followed by a post-C7 DQ sequence to prepare and then reconvert DQ coherences. Experimentally optimized DQ excitation time = 2.02 ms; spinning speed = 7.937  $\pm$  0.005 kHz; \* = spinning sidebands.

**Table 2.** Phosphine Concentrations on Zeolite HY

	loading level <sup>a</sup>	physisorbed	singly protonated	doubly protonated
Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub>	4	<1%	40%	60%
	8	<1%	59%	41%
	12	3%	60%	37%
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub>	4	2%	7%	91%
	8	13%	10%	77%
	12	22%	26%	53%
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>6</sub> PPh <sub>2</sub>	4	<1%	1%	98%
	8	3%	4%	94%
	12	3%	7%	90%

<sup>a</sup> Number of diphosphine molecules per unit cell of HY.

NMR spectrum of the  $n = 1$  sample contains intense off-diagonal peaks at (14, –14) and (–28, –14), which connect the SQ resonances at –28 and 14 ppm (Figure 2). Two diagonal peaks are observed at (8, 16) and (–1, –2), but there is no peak at (–28, –56). These results indicate that the resonance at –28 ppm is due to the nonprotonated end of the singly protonated diphosphine. The protonated end of this diphosphine gives rise to a broad resonance with a maximum at 14 ppm, while the doubly protonated phosphines resonate at 8 and –1 ppm. The distributions in chemical shifts arise from different local environments inside the zeolite.

$^{31}\text{P}$  NMR spectra were acquired as a function of phosphine loading level (Figures S2–S4), and the intensities of the different resonances and, thus, concentrations of the different phosphine molecules and ions are reported in Table 2. Although there are always more Brønsted acid sites than phosphorus atoms at all loading levels, a significant fraction of the diphosphines are singly protonated for  $n = 1$ , while for  $n = 3$  and 6, more than 90% of diphosphines are doubly protonated at the lowest loading level. The  $n = 6$  data indicate that there are at least 12 pairs of Brønsted acid sites/unit cell whose conjugate bases are approximately 9 Å apart or less. On the basis of the  $n = 3$  data, there are only six pairs of strong Brønsted acid sites whose conjugate bases,  $\text{O}_{\text{CB}}$ , are approximately 6 Å apart or less. The distance of 6 Å corresponds to the separation between  $\text{O}_{\text{CB}1}$  and  $\text{O}_{\text{CB}2}$  oxygen atoms in the zeolite framework species,  $\text{O}_{\text{CB}1}\text{--T--O--T--O}_{\text{CB}2}$ , where T–O– is the Si/

Al–O linkage. For  $n = 1$ , only 3–4 pairs of strong acid sites exist per unit cell. Now, the doubly protonated phosphine will only be able to bind to either the same T atom in environments such as  $\text{Al--O}_{\text{CB}1}\text{--Si--O}_{\text{CB}2}\text{--Al}$  or to two O4 oxygen atoms in the same 4-ring because of the short P–P distance. Thirty-eight percent of all Si atoms are connected to two or more Al atoms in the sample investigated here, indicating that the concentration of  $\text{Al--O}_{\text{CB}1}\text{--Si--O}_{\text{CB}2}\text{--Al}$  sites is not the limiting factor in allowing double protonation. Only a subset of these silicon sites will contain protons bound to both  $\text{O}_{\text{CB}1}$  and  $\text{O}_{\text{CB}2}$ , prior to phosphine sorption (since the protons can bind to any of the four oxygen atoms coordinated to Al). Thus, the results suggest that not all the  $\text{O}_{\text{CB}}$  sites are sufficiently basic to allow proton migration from a nearby Brønsted acid proton to the phosphine molecule, and subsequent H-bonding to  $\text{O}_{\text{CB}}$ , to occur.  $^1\text{H}$  2D DQ experiments of the bare zeolite along with computer modeling of the probe molecule–zeolite interactions are in progress to explore these hypotheses.

In conclusion, we have presented results for a series of basic probe molecules that are sensitive to not only distances between acid sites but also the acidity of the site itself and the basicity of the conjugate base that represents the sorption site for the protonated phosphine. Applications of the approach to a wider range of materials with both Lewis and Brønsted acidity and with much lower concentrations of acid sites are currently underway.

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**Supporting Information Available:** Procedures used to prepare the samples, details of the NMR experiments, and the NMR spectra analyzed to produce the data reported in Table 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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