

## Proton Acidity and Proton Mobility on Alumina Surfaces: Reply to H. Knözinger

Knözinger raises an interesting point concerning the apparent inconsistency between my work on measuring Brønsted acid sites on the alumina surface by a deuterated pyridine–nuclear magnetic resonance method (1) and his infrared studies on the same subject (2). I believe we could agree that any Brønsted sites found on the alumina surface would be weak in comparison to those found on some silica–alumina surfaces. It is probably also true that the formation of the pyridinium ion ( $\text{PyH}^+$ ) depends not on the absolute pressure of pyridine in contact with the surface, but on the relative pressure ( $P/P_0$ ). In our work, the Brønsted sites were found when the alumina surface was in contact with a deuterated pyridine pressure equal to the vapor pressure of deuterated pyridine at  $0^\circ\text{C}$ . This is equal to about 6 Torr of pressure or a  $P/P_0$  of about 0.25 with the sample at  $25^\circ\text{C}$ . This assumes the vapor pressure of deuterated pyridine is equal to that of regular pyridine.

Knözinger and Kaerlein (2) measured the infrared spectrum of alumina in contact with pyridine vapor at a pressure of 27 Torr. It was inferred in Ref. (1) that they had evacuated the sample. This was my error. They did, however, heat the sample. At temperatures above the boiling point of pyridine ( $115.4^\circ\text{C}$ ), the pressure of pyridine used would be equivalent to a  $P/P_0$  of less than 0.04. A remarkable increase in surface acidity

would have had to occur before Brønsted sites could be seen under these conditions.

The failure to detect Brønsted acidity with the sample at  $43^\circ\text{C}$  [the lowest temperature reported in Ref. (2)] is more difficult to explain. This failure could be related to the infrared spectrum of pyridine on the alumina surface. The infrared shows bands due to  $\text{PyH}^+$  at 1540, 1490, and  $1680\text{ cm}^{-1}$  (3). Only the  $1540\text{ cm}^{-1}$  band is not overlapped by a band from pyridine adsorbed on a Lewis acid site. Moreover, the  $1540\text{ cm}^{-1}$  band is by far the least intense one in this region of the spectrum (4). It is possible that the infrared method is not very sensitive for measuring Brønsted sites in the presence of large amounts of Lewis acidity. The ratio of Brønsted to Lewis acidity reported in Table 1 of Ref. (1) is 1 to 16.7.

Although Knözinger presents an interesting interpretation of the results given in Ref. (1), I do not believe his interpretation can account for the presence of the narrow line which was used as a measure of Brønsted acidity. Knözinger appears to be saying that the deuterated pyridine is held to the alumina surface by hydrogen bonds between the nitrogen of the deuterated pyridine and the hydrogen of the surface hydroxyl groups. This is undoubtedly true under some conditions, as, for example, alumina in equilibrium with deuterated pyridine at room temperature ( $\approx 25$  Torr of pyridine pressure). These conditions were shown in Fig. 6 of Ref. (1)

to produce a narrow line in the deuterium NMR spectrum of the sample. These conditions cannot be used to measure Brønsted acidity. Instead, the pressure of deuterated pyridine is reduced to about 6 Torr. Under these conditions, the sample does not show the presence of the narrow NMR line in the deuterium NMR spectrum [see Fig. 7 of Ref. (1)] and contains no physically adsorbed pyridine, at least as defined in the context of a narrow NMR line in the proton NMR spectrum of the sample.

Knözinger may be correct in stating that pyridine which is hydrogen bonded to the surface hydroxyls would increase the mobility of the surface protons. It is also correct to say that this increased mobility would lead to a "narrowing" of the NMR signal. But, since these protons would still be rapidly exchanging with the rest of the chemically bound protons in the sample, this increased mobility would lead to a "narrowing" of the broad NMR line due to the chemically bound protons in the alumina, i.e., the line several gauss wide shown in Fig. 5

of Ref. (1). It would not result in the formation of a narrow line superimposed on that broad line. The same argument holds true for the interpretation of the proton NMR signal of well-crystallized boehmite proposed by Fripiat and Touillaux (5). This subject was discussed in a previous paper (6).

## REFERENCES

1. Pearson, R. M., *J. Catal.* **46**, 279 (1977).
2. Knözinger, H., and Kaerlein, C. P., *J. Catal.* **25**, 436 (1972).
3. Scokart, P. V., Declercq, F. D., Sempels, R. E., and Rouxhet, P. A., *J. Chem. Soc. Faraday Trans. 1*, 359 (1977).
4. Parry, E. P., *J. Catal.* **2**, 371 (1963).
5. Fripiat, J. J., and Touillaux, R., *Trans. Faraday Soc.* **65**, 1236 (1969).
6. Baker, B. R., and Pearson, R. M., *J. Catal.* **33**, 265 (1974). p. 265.

R. M. PEARSON

*Kaiser Aluminum & Chemical Corporation  
Center for Technology  
Pleasanton, California 94566*

*Received February 7, 1978*