# LETTERS TO THE EDITORS

Protonic Acidity and Proton Mobility on Alumina Surfaces

In a recent paper Pearson (1) reported the detection of Brønsted acid sites on aluminum oxide surfaces using deuterated pyridine as a probe and wide-line nuclear magnetic resonance as the experimental technique. It is well known that the pyridinium ion PyH+ has never been detected on aluminas by infrared spectroscopy (2). Pearson interpreted this failure as due to the low sensitivity of the infrared technique. Furthermore he correctly stated that infrared spectra had mostly been measured after evacuation of the adsorbed pyridine at elevated temperature, a procedure which could remove the pyridine held by Brønsted sites in the form of PyH+. In this connection Pearson referred to a paper by Knözinger and Kaerlein (3). I would like to point out that the citation of our paper in this respect was incorrect. The aim of our work was to test whether pyridine formed PyH+ on alumina surfaces at elevated temperatures in the presence of pyridine vapor. The result was negative, i.e., no PyH+ could be detected in the infrared spectra at 3.6×10^3 N m^{-2} and at temperatures up to 550 K (3). It may be mentioned that Gay and Liang (4) using ^{13}C nuclear magnetic resonance were not able to detect protonated pyridine on aluminas either.

The Brønsted acid sites postulated by Pearson were detected only indirectly by the appearance of a narrow proton NMR line in the presence of weakly adsorbed pyridine. This observation is interpreted as being due to the formation of PyH+.

It is known that weakly adsorbed pyridine is bound via H bonds between the low-frequency surface hydroxyl groups as donors and the pyridine nitrogen as an acceptor: O–H···N (2). The hydroxyl proton in such H bonds is located in an asymmetric double minimum potential well. The exact form of this potential is modified by the local surface electric field gradient and the geometry of the H bond. The proton can fluctuate between the two equilibrium positions:

$$O–H \cdots N \rightleftharpoons O^{2-} \cdots H^+N.$$
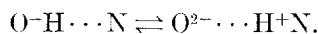
The probabilities of the proton jumps and the relative residence times at the hydroxyl oxygen or the pyridine nitrogen strongly depend on the detailed form of the potential well (5). Proton transfer between such asymmetric H bonds involving O and N has recently been discussed by Lindemann and Zundel (6). It may therefore be suggested that the formation of H bonds between surface OH groups and pyridine induces an increased "mobility" of the hydroxyl proton. This leads to a narrowing of the nuclear magnetic resonance signal, provided the proton jump frequency is high as compared to the NMR time scale, which is most probably the case. This may be an alternative interpretation of Pearson's results. The observation of a narrow proton magnetic resonance line in boehmite (γ-AlOOH) has analogously been assigned to proton jumps between lattice oxygen ions (7). Moreover, the formation of the H bond and the resulting vibrational normal

modes of the surface adduct may also facilitate the lateral motion of a proton, i.e., the transfer from one surface oxygen to a neighboring one. Such a mechanism might account for the "increased Brønsted acidity" with increasing activation temperature as described by Pearson (1). The number of O^{2-} neighbors of a surface OH group increases as the degree of hydroxylation is reduced; thus, the number of strong acceptor sites surrounding an OH group grows and the proton transfer with the aid of pyridine may be facilitated, whereby the correlation time and consequently the line width will be reduced. Finally, the anharmonicity of an OH potential can probably be increased by lateral interactions with coordinately bound pyridine, which should also increase the mobility of the proton.

One may argue that the proton transfer in an $OH \cdots N$ bond as discussed above would lead to the formation of PyH^+. Regarding the relevance of such proton transfer processes for catalytic reactions, the time scale of various consecutive processes has to be considered. Fripiat (8) suggested four time constants, the relative values of which determine the probability of a catalytic process: (i) lifetime of a protonated site; (ii) residence time of an adsorbed molecule; (iii) lifetime of the protonated molecule; (iv) time required for the chemical transformation. The residence time of an adsorbed molecule corresponds to the lifetime of an $OH^- \cdots N$ H bond, and the lifetime of the protonated molecule, i.e., of the PyH^+, depends on the form and relative depth of neighboring minima in the potential well of the $OH \cdots N$ bond. This potential is most probably asymmetric, favoring the equilibrium posi-

tion at the surface oxygen. The residence time of the proton at the pyridine nitrogen should thus be relatively small. The number of PyH^+ of the order of magnitude of 10^{17} m^{-2}, as given by Pearson (1), should be detected in the infrared range provided the average lifetime of the species is of the order of 10^{-12} sec. The lifetime of the protonated form of other molecules such as hydrocarbons with weaker H-bond acceptor strength must be still lower due to the higher asymmetry of the double minimum potential well. The experimental observations of Pearson may therefore be discussed in terms of an increased mobility of surface protons which is induced by the adsorbed pyridine, rather than in terms of protonic acidity which accounts for carbonium ion reactions on the surface of aluminas.

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HELMUT KNÖZINGER

Institut für Physikalische Chemie
Universität München
Sophienstrasse 11
8000 München 2
Germany