interaction of $C_6H_{12}$ with the catalytic surface was a dehydrogenative chemisorption producing adsorbed $H_2$, which, in the presence of $C_6H_6$, induced the hydrogenative desorption of the latter in the form of $C_6H_{12}$. Thus, reaction (1) may be visualized to occur as a sequence of two steps, namely,

$$C_6H_{12}(g) \rightarrow C_6H_6(g) + 6H(s) \qquad (1a)$$

$$^*C_6H_6(g) + 6H(s) \rightarrow {}^*C_6H_{12}(g) \qquad (1b)$$

Support for this view was obtained by initially feeding to the reactor $C_6H_{12}$ only. Under these conditions (200°C) the formation of $H_2$ was detected. Introduction of $C_6H_6$ in the inlet stream totally suppressed the appearance of gas-phase $H_2$. The results of Table 1 indicate that Pt is the most active of the catalysts reported. This conclusion is in agreement with the large body of experimental results on the catalytic hydrogenation of benzene. This is not unexpected since kinetically reaction step (1b) [or the reverse of reaction step (1a) ] represents one stage of the overall hydrogenation reaction of benzene.

During the occurrence of reaction (1) a chemical equilibrium between gas and surface phases is established. The establishment of this equilibrium is supported by the experimental observations of constant reaction conversion for periods of several days of operation. Similarly the ratio of benzene to cyclohexane was found invariant in the reactor space and in time. Thus reaction (1) may be used as a kinetic tool for the study of the rate of hydrogen transfer at catalytic surfaces under conditions of chemical equilibrium. The chemical potential of the reaction intermediate, adsorbed $H_2$, is a function of the ratio of benzene to cyclohexane at equilibrium. This ratio is constant and known during the occurrence of reaction (1). Thus, by obtaining experimental rate results at various ratios of benzene to cyclohexane, the influence of the chemical potential of adsorbed $H_2$ upon the rate of reaction (1) may be brought to light. Since adsorbed $H_2$ is the common intermediate of the catalytic hydrogenation of aromatics, we conclude that reaction (1) represents a useful and interesting kinetic tool for the study and classification of catalytic behavior in the hydrogenation of aromatic hydrocarbons.

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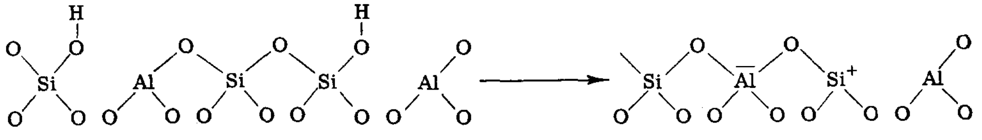
# The Ratio of Absorption Coefficients of Pyridine Adsorbed on Lewis and Brönsted Acid Sites

Spectroscopic studies of adsorbed bases, in particular pyridine, have become well established techniques for investigating the surface acidity of catalysts (*1–6*). Brönsted and Lewis acidity can readily be detected and distinguished. In many cases, it is of interest not only to determine the type of acid sites but also their relative numbers. Specific absorption bands in the spectrum of chemisorbed pyridine near 1545 and 1450 $cm^{-1}$ can be assigned to pyridine adsorbed on Brönsted and Lewis acid sites, respectively. An absorption band near 1490 $\text{cm}^{-1}$ is indicative of both types of acid sites.

The intensity of an absorption band is related to the concentration of the absorbing species by Beer's Law: Intensity ($I$) = $\epsilon cd$ where $c$ is the concentration of absorbing species; $d$, the thickness of absorbing species; and $\epsilon$, a constant for any given species, the absorption coefficient. If $\epsilon$ has the same value for both the species, a measurement of the ratio of absorption band intensities would give the ratio of the acid site concentrations. This assumption is not justified since fundamentally different modes of bonding of pyridine to the surface are involved. Basila and co-workers (*2*, *7*) have examined this problem. In their second report, they show that their first calculations contained an erroneous assumption and derive a new equation for the ratio of acid sites. This relationship depends on the establishment of the ratio $\epsilon_{1490}^{\text{Lewis}}/\epsilon_{1450} = 0.25$ from studies of potassium poisoned silica-alumina. For the 1490-$\text{cm}^{-1}$ band, they estimated the ratio of the extinction coefficients of pyridine on Brönsted acid sites to pyridine on Lewis acid sites $\epsilon_{1490}^{\text{Brönsted}}/\epsilon_{1490}^{\text{Lewis}}$ to be $6.0 \pm 0.9$. Hughes and White (*3*) have recently obtained the value of 5.8 by combining data from several catalysts.

While the assumptions behind these derivations are probably sound, they are not completely certain, for example, $\epsilon_{1490}^{\text{Lewis}}/\epsilon_{1450}$ may vary from catalyst to catalyst. The ratio of the absorption coefficients and hence the ratio of Brönsted and Lewis acid sites can be determined from measurements on the same catalyst calcined at different temperatures.

The variation of absorption band intensities of the 1545- and 1450- $\text{cm}^{-1}$ absorption bands of chemisorbed pyridine on zeolites has been reported previously (*3*, *6*, *8*). The conversion of Brönsted acid sites into Lewis acid sites has been suggested by several workers to follow the scheme:



Thus two Brönsted acid sites are converted into one Lewis acid site. The sum of twice the Lewis acid site concentration plus the Brönsted acid site concentration should remain constant and only their ratio should change with temperature.

Thus for temperatures $T'$ and $T''$, the following equations can be written: No. of Brönsted acid sites + 2 × No. of Lewis acid sites = constant. From Beer's Law,

$$\frac{I_{\text{B}}^{T'}}{\epsilon_{\text{B}}} + 2\frac{I_{\text{L}}^{T'}}{\epsilon_{\text{L}}} = \text{constant}$$

and

$$\frac{I_{\text{B}}^{T''}}{\epsilon_{\text{B}}} + 2\frac{I_{\text{L}}^{T''}}{\epsilon_{\text{L}}} = \text{constant}$$

then,

$$\frac{2(I_{\text{L}}^{T'} - I_{\text{L}}^{T''})}{\epsilon_{\text{L}}} = \frac{I_{\text{B}}^{T''} - I_{\text{B}}^{T'}}{\epsilon_{\text{B}}}$$

where $I_{\text{L}}$ and $\epsilon_{\text{L}}$ are the intensity and absorption coefficient of the 1450-$\text{cm}^{-1}$ band and $I_{\text{B}}$ and $\epsilon_{\text{B}}$ are the intensity and absorption coefficient of the 1545-$\text{cm}^{-1}$ band.

Thus,

$$\frac{\epsilon_{\text{L}}}{\epsilon_{\text{B}}} = \frac{2(I_{\text{L}}^{T'} - I_{\text{L}}^{T''})}{I_{\text{B}}^{T''} - I_{\text{B}}^{T'}}$$

Hence by making the pyridine absorption studies after calcination of a catalyst at two temperatures $\epsilon_{\text{L}}/\epsilon_{\text{B}}$ can be determined and the acid site ratio is given by

$$\frac{(\text{Lewis sites})}{\text{Brönsted sites}} = \frac{I_{\text{L}}}{I_{\text{B}}}\frac{\epsilon_{\text{L}}}{\epsilon_{\text{B}}}$$

Figure 1 shows data obtained for magnesium hydrogen Y zeolite as a function of calcination temperature (*8*). The data were obtained by measuring the pyridine remaining chemisorbed after evacuation at 250°C for 2 hr. Taking values of the intensity measured after calcination at 500° and 700°C, $\epsilon_{\text{L}}/\epsilon_{\text{B}} = 1.1$. Taking other pairs of temperatures and also evaluating the data

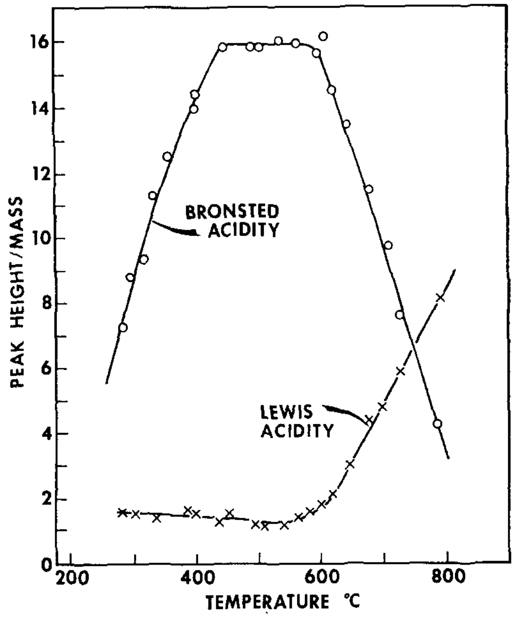


Fig. 1. Intensities of absorption bands of chemisorbed pyridine on Brönsted and Lewis acid sites on magnesium hydrogen Y zeolite.

reported for ammonium Y zeolite (*6*), values of $\epsilon_L/\epsilon_B = 1.1 \pm 0.2$ are obtained. Hence for equal numbers of Brönsted and Lewis acid sites, the 1450-cm$^{-1}$ band should be 1.1 times as intense as the 1545-cm$^{-1}$ band. Results from the simple $\epsilon_L/\epsilon_B = 1.1$ relationship can be compared with the results calculated from Basila and Kantner's relationship.

For American Cyanamid Aerocat Triple A alumina, Basila and Kantner (*7*) found a band ratio $I_{1450}/I_{1545}$ of 10.5 which gave by their formula a site ratio of Lewis/Brönsted of 6. Using the above relationship, a ratio of 9.5 is obtained. For an ammonium Y zeolite calcined at 500°C, band intensities were observed as follows: 1545 cm$^{-1}$, 0.16; 1490 cm$^{-1}$, 0.22; and 1450 cm$^{-1}$, 0.12. Using Basila and Kantner's formula (*7*) (Lewis acid sites)/(Brönsted acid sites) = 0.9 and by the above formula, 0.7.

Thus, this simple approach to the determination of acid site ratios gives results consistent with those obtaeined by less direct methods.

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