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Determination of the Nature of Catalyst Acid Sites by Infrared Spectroscopy

This note aims to report a new possibility for the evaluation of Lewis acidity of high alumina catalysts and carriers. The method is founded on the measurement of the infrared *symmetrical* deformation band of ammonia. Up to now, only the N–H stretching or the asymmetrical deformation bands of ammonia had been used (*1–3*).

Silica-alumina catalysts were prepared by hydrolysis of aluminum isopropoxide and ethyl silicate, according to the procedure described by Leonard *et al.* (*4*) and calcined at 500°C for 16 hr in a muffle oven. The sample film, held in a cell fitted with NaCl windows, was heated under high vacuum ($\leqslant 10^{-5}$ mm Hg) at 400°C for at least 2 hr. Ammonia was introduced at this temperature and the sample was slowly brought to room temperature, while a constant ammonia pressure of 50 mm Hg was maintained in the cell. After equilibrium was established, the film was evacuated overnight at 25°C. The sample was then heated successively at 100°, 200°, and 300°C, and finally water vapor from the atmosphere was admitted into the cell. The spectra were obtained by a Beckman I.R. 4 spectrophotometer fitted with sodium chloride or calcium fluoride optics.

The asymmetrical deformation bands are observed for ammonia at 1630–1620 cm^{-1}, for ammonium at 1480–1475 cm^{-1} in alumina-rich samples, and at 1450–1440 cm^{-1} in substances of low alumina contents. For example, the ammonium deformation band is centered at 1444 cm^{-1} for a silica-alumina containing 85% silica, whereas for pure alumina it is situated at 1478 cm^{-1}. At increasing silica content the shoulder at 1444 cm^{-1} which is very small for samples containing 5% silica, becomes more important, so as to present a single band for 85% silica catalysts.

In the 1350–1200 cm^{-1} spectral range, a strong and rather broad band appears in samples rich in alumina and exposed to NH_3. The frequency of this band shifts to higher values when the catalyst is heated. It may also be present in substances of high silica content, but the overlapping with Si–O vibrations does not permit its characterization. This band coincides with that of the symmetric deformation of ammonia reported for ammine coordination complexes (*5*) which is known to be very sensitive to the electronic character of the metal. Wilmshurst (*6*) has established a linear relationship between the electronegativity of the metal in the ammine complexes and the square of the symmetric deformation frequency. By applying the Wilmshurst equation to the ammonia-treated samples and relating the electronegativity to catalyst acidity, a very simple method for the determination of the acid strength is obtained. From the relationship observed by Wilmshurst, it follows that the electronegativity of the aluminum Lewis site should lie between 1.8 and 2.4. As compared with the electronegativity value com-

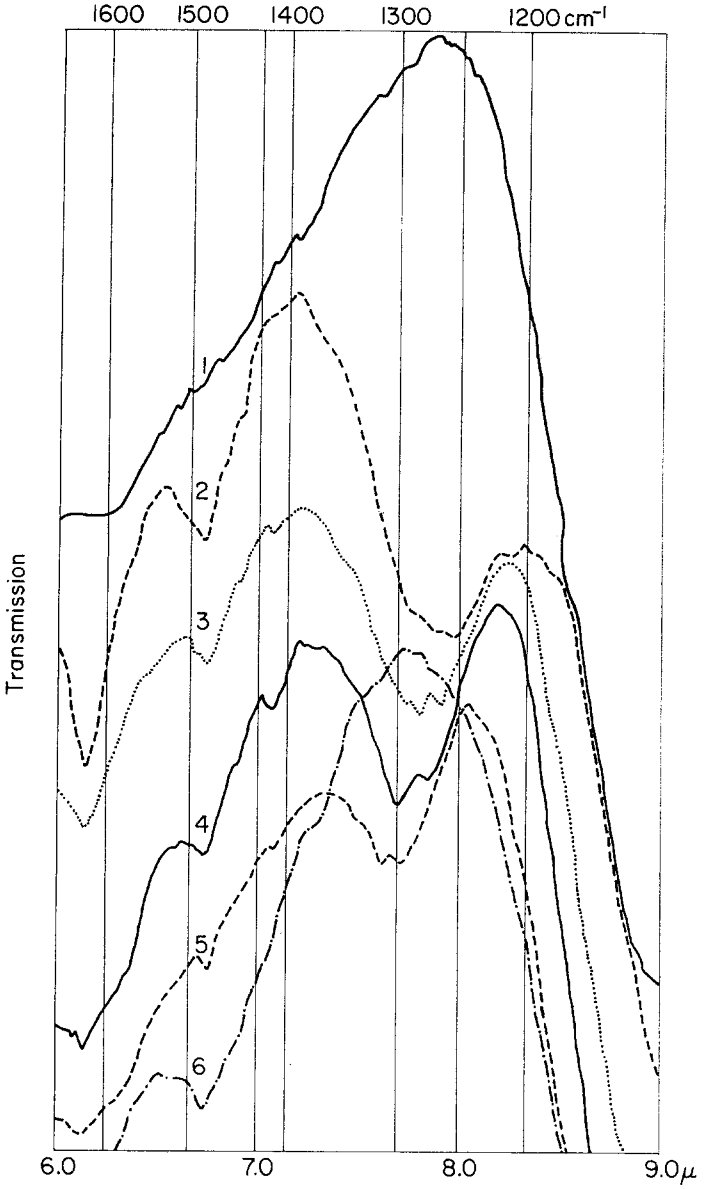

FIG. 1. Spectra of a silica-alumina sample containing 5% SiO_2: 1, Pretreated at 400°C under vacuum (2 hr). 2, Adsorption of ammonia at 50 mm Hg and 400°C; sample cooled to room temperature at a constant ammonia pressure; spectrum recorded after evacuation at 25°C for 15 hr ($\leqslant 10^{-5}$ mm Hg). 3, Spectrum obtained after evacuation of 2 at 100°C for 2 hr ($\leqslant 10^{-5}$ mm Hg). 4, Spectrum obtained after evacuation of 3 at 200°C for 2 hr ($\leqslant 10^{-5}$ mm Hg). 5, Spectrum obtained after evacuation of 4 at 300°C for 2 hr ($\leqslant 10^{-5}$ mm Hg). 6, Introduction of water at room temperature.

puted for the element by Pauling (7) i.e., 1.5, it may be concluded that the increase due to the formation of a Lewis site ranges from 0.3 to 0.9 electronegativity units.

As can be seen in Fig. 1, ammonia adsorbed on Lewis sites produces a band between 1350 and 1200 cm^{-1}, the frequency of which depends on the strength of the sites. When the outgassing temperature is increased, the ammonia molecules adsorbed on weak acid centers are released, resulting in a frequency shift to higher values. For example, the frequency for the 5% SiO_2 sample shifts from 1250 cm^{-1} at 25°C to 1311 cm^{-1} at 300°C. For pure alumina the corresponding values range between 1210 and 1300 cm^{-1}, according to the pretreatment conditions.

The evaluation of the number of Lewis and Bronsted sites has usually been based on the integrated intensity of the asymmetrical deformation bands. For a relative comparison of both types of acidity, the ratio of the absorption coefficients $R = \epsilon_{NH_4^+}/\epsilon_{NH_3}$ has to be estimated. From our determination, it appears to be of the order of magnitude of 7. This implies that the asymmetrical band of NH_3 between 1630 and 1620 cm^{-1} is often very small and that the determination of the relative number of Lewis sites is not accurate. On the contrary, the symmetrical deformation band between 1350 and 1200 cm^{-1} (curve 5, Fig. 1) is several times greater than the asymmetrical deformation band for ammonium after conversion of NH_3 into NH_4^+ (curve 6) and, *a fortiori* than that of NH_3. Therefore, the symmetrical deformation mode due to ammonia on Lewis sites is an easier tool for studying the surface acidity of aluminas and silica-aluminas rich in Al_2O_3.

Curve 6 also clearly shows that the transformation of ammonia into ammonium is quite complete when the sample is exposed to the atmospheric moisture. This could not be demonstrated earlier because of the superposition of the deformation bands of ammonia and water in the 1650–1600 cm^{-1} range.

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The Isomerization of *n*-Butenes over a Deuterated Ion Exchange Resin

Extensive studies have been carried out on the active sites of solid acid catalysts, such as silica-alumina. On such catalyst surfaces a variety of acid sites has been observed and a catalyst with a homogeneous acid surface would be helpful in