Modification of the Surface Acidity of γ-Alumina

Catalytic activity is considered to depend strongly upon the surface acidity (*1*). Titration with amines and indicator adsorption have been used to determine the surface acidity of oxide catalysts (*2, 3*). Electronic spectra of adsorbed Hammett indicators (*4*), photoacoustic spectroscopy (*5*), and ir spectroscopy (*6, 7*) are also currently employed to estimate the acid sites on surfaces of oxides and supports.

We report here the modification of the acid sites on surfaces of several samples of γ-Al$_2$O$_3$ by acid treatment. We have carried out a quantitative determination of their acid site content by means of a spectrophotometric method (*8, 9*) using pyridine and quinoline as titrants. All chemicals were reagent-grade, samples were prepared from a Girdler γ-Al$_2$O$_3$ with a BET surface area of 188 m^2 g^{-1} and a pore volume of 0.39 cm^3 g^{-1}. γ-Al$_2$O$_3$ samples (4.5 g) were treated with distilled water (60 cm^3) at pH 7.00 in the case of nonprotonated γ-Al$_2$O$_3$, or with standardized solutions of HNO$_3$ (60 cm^3) at different concentrations in the case of protonated γ-Al$_2$O$_3$, always with stirring for 12 h. Suspensions were filtered, and solids were dried under vacuum at 393 K for 12 h. (Drying at temperatures between 393 and 723 K resulted in similar acid site content of equal or lower pK$_a$'s than pyridine or quinoline.) These dry and protonated γ-Al$_2$O$_3$ samples modify the physical characteristics and catalytic activity of supported metal catalysts for ammonia synthesis by comparison with a dry nonprotonated γ-Al$_2$O$_3$ (*10*).

The quantitative determination of the acid site content of either nonprotonated γ-Al$_2$O$_3$ or the protonated γ-Al$_2$O$_3$ was followed by uv spectrophotometry with cyclohexane solutions of pyridine or quinoline as titrants. As soon as adsorption of the titrant

upon the solid remained constant, formation of a monolayer of base upon the acid sites with equal or lower pK$_a$'s was assumed (*8, 9*).

Applying the equation of a Langmuir isotherm:

$$C/X = 1/(bX_\mathrm{m}) + C/X_\mathrm{m} \qquad (1)$$

where C = concentration of nonadsorbed base (measured by uv spectrophotometry) in equilibrium with the adsorbed base upon the solid, X = adsorbed base per gram of solid, b = constant, X_m = adsorbed base per gram of solid in monolayer conditions (assuming all of the acid sites are occupied by the titrant), we plotted C/X versus C.
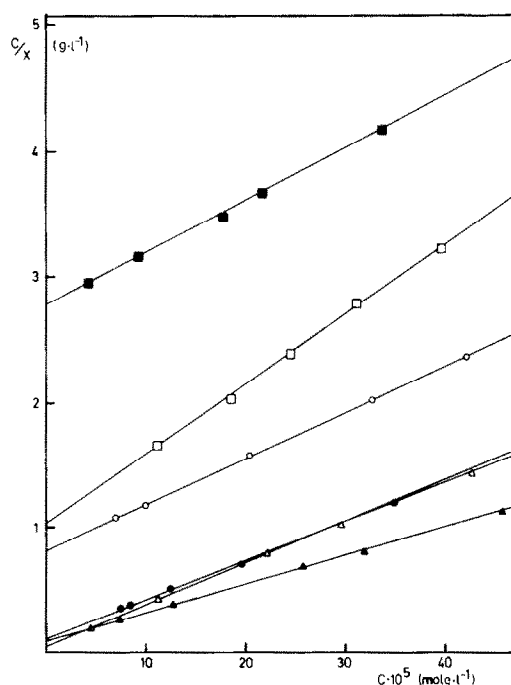

FIG. 1. Titration of acid sites of pretreated γ-Al$_2$O$_3$ samples, plotted according to Eq. (1). γ-Al$_2$O$_3$ was pretreated with: □, distilled H$_2$O; ○, 500 μmole H$^+$ · g^{-1} γ-Al$_2$O$_3$; △, 5000 μmole H$^+$ · g^{-1} γ-Al$_2$O$_3$. Solid symbols = pyridine, open symbols = quinoline.

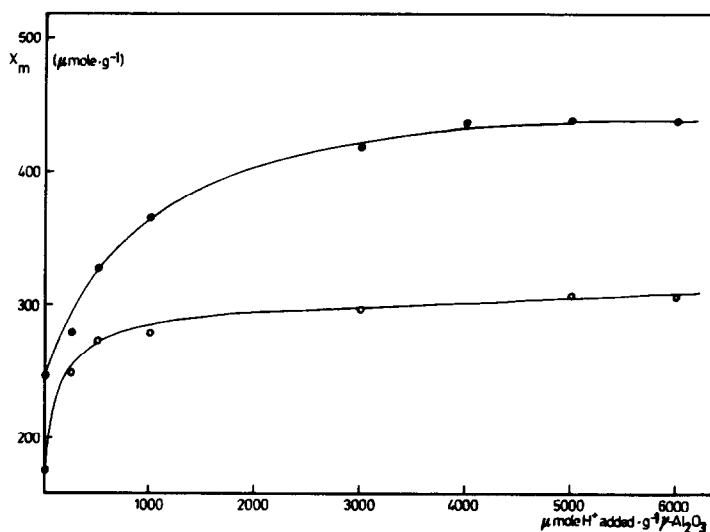FIG. 2. Plot of X_m against μmole H$^+$ added to γ-Al$_2$O$_3$ samples, using the following titrants: ● pyridine, ○ quinoline.

Straight lines adjusted by least squares with a correlation coefficient higher than 0.999 were obtained, as shown in Fig. 1.

The Langmuir model assumes that adsorbing sites of the support are homogeneous and no interaction between adsorbed molecules takes place on the surface of the support. In our case, we are dealing with heterogeneous acid sites, of which the more acid ones are first occupied by the titrating amine. However, we consider that the acid sites with equal or lower pK_a's to that of the amine are titrated when equilibrium of adsorption is achieved. X_m would then be a measure of the acidity of the solid surface, and the value (bX_m) should grossly measure the strength of the interaction between the amine and the acid site. Values of the X_m obtained from Fig. 1 were plotted against the total micromoles of acid added per gram of solid, and Fig. 2 shows the hyperbolic curves obtained, where the plateau indicates the maximum value of X_m for each amine. The different values of X_m for pyridine and quinoline are in accordance with their different sizes and donor strengths.

These results are preliminary to a work on acid-modified γ-Al$_2$O$_3$ as a support for the preparation of ammonia synthesis catalysts.

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