Effect of Moisture & Particle Size on the Acid Strength Distribution of Solids by Non-aqueous Titrations

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The effect of moisture and particle size on the [acid] and acid strength distribution of silica-alumina have been studied by non-aqueous titration method employing Hammett indicators. Stronger acid sites are poisoned appreciably by moisture and acidity also varies with particle size.

THE non-aqueous titrations reported first by Tamele[1], Walling[2] and Johnson[3] were modified by Benesi[4] and these have been used extensively not only to determine the total amount of acids but also the acid strength distribution spectrum of the solid acids[5]. Atmospheric moisture can change the acidic properties of a solid to a considerable extent. The effect of moisture and particle size on the acidity constitute an important aspect to be examined. Therefore, the effect of these factors on the [acid] and acid strength distribution of silica-alumina [Davison grade 979; SiO_2, 87·0%; Al_2O_3, 13·0%; surface area, 400 cm^2/g, pore volume, 1·0 ml/g] have been studied using Benesi's[4] procedure and employing *n*-butylamine as the titrant and the following Hammett indicators[6]: Neutral red (*pka*, +6·8), *p*-ethoxychrysoidin-monohydrochloride (*pka*, +5·0), *p*-dimethylaminoazo benzene (*pka*+3·3), 2-amino-5-azo-toluene (*pka*, +2·0), dicinnamal acetone (*pka*, −3·0), benzalacetophenone (*pka*, −5·6) and anthraquinone (*pka*, −8·2).

Effect of moisture — Samples were kept in an atmosphere of 100% humidity at 25·0° for 0·5, 1·0, 2·0, 6·0 and 16·0 hr and their acidity was measured. It is evident from Table 1 that for 0·5 hr exposure of the sample all sites of medium and strong acid strengths (*pka* −3·0 to −8·2 and < −8·2) are poisoned to a considerable extent, while there is an increase in the concentration of weak acid sites (*pka* +6·8 to −3·0). This increase is at the expense of some stronger acid sites which are being converted into weaker ones. On further increasing the exposure time, the stronger sites are unaffected but the concentration of weaker sites is further suppressed till it becomes almost constant indicating an optimum poisoning, after which no substantial poisoning of sites was observed.

Effect of particle size — Samples of silica-alumina of different particle size were collected and their acid strength distribution determined. A perusal of the data in Table 2 reveals that the concentration of weak and very strong acid sites (*pka* +6·8 to +2·0 and <−8·2) increases continuously with decreasing particle size and reaches a limiting value at the mesh size 100-200 ASTM below this size the concentration of all the sites is practically constant. This variation of acidity values with particle size at higher range is presumably due to the non-uniform adsorption of *n*-butylamine on the larger particles. On the other hand at lower range of particle size (100-200 and <200 mesh) the distribution is uniform. Therefore particle size should be <0·074 mm (<200 mesh) to ensure reproducibility and accuracy of results.

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TABLE 1 — EFFECT OF HUMIDITY ON THE ACIDITY OF THE SILICA-ALUMINA SAMPLE (PARTICLE SIZE <0·074 mm)

Time of exposure (hr)	*n*-Butylamine titre (mmoles/g) at *pKa*					Total
	+6·8 to +2·0	+2·0 to −3·0	−3·0 to −5·6	−5·6 to −8·2	<−8·2	
0·0	0·27	0·00	0·00	0·0	0·23	0·50
0·5	0·30	0·13	0·05	0·0	0·00	0·48
1·0	0·25	0·10	0·05	0·0	0·00	0·40
2·0	0·23	0·07	0·05	0·0	0·00	0·35
6·0	0·20	0·10	0·00	0·0	0·00	0·30
16·0	0·20	0·05	0·00	0·0	0·00	0·25

TABLE 2 —EFFECT OF PARTICLE SIZE ON THE ACIDITY OF THE SILICA-ALUMINA SAMPLE

Mesh size (ASTM)	Particle size (mm)	*n*-Butylamine titre (mmoles/g) at *pKa*					Total
		+6·8 to +2·0	+2·0 to −3·0	−3·0 to −5·6	−5·6 to −8·2	<−8·2	
30-50	0·595-0·297	0·10	0	0	0	0·10	0·20
50-100	0·297-0·194	0·15	0	0	0	0·20	0·35
100-200	0·194-0·074	0·25	0	0	0	0·25	0·50
<200	<0·074	0·25	0	0	0	0·25	0·50