

CHAPTER-III

STUDIES ON SPHEROIDAL GAMMA ALUMINA

III.1 INTRODUCTION

Alumina is a potential material for use as adsorbent, catalyst, and catalyst support. Numerous investigations have been carried out on the use of alumina as catalysts and catalyst supports. Eventhough alumina itself catalyses a number of reactions, the use of alumina as a catalyst support is of more interest to a catalyst researcher. Table No.III.1 identifies major catagories of catalyst applications where alumina has proven itself as a suitable catalyst or support. The selection of a material for use as a catalyst support depends on a number of technical criteria, its abundance and availability with desirable and reproducible characteristics at reasonable cost. The technical criteria would include the following inherent properties, namely:

- a. Purity of crystalline phase, crystallinity and crystallite size,
- b. Appropriate surface area and other textural properties like pore volume and pore size distribution,
- c. Surface acidity, and
- d. Physical strength.

Of the various supports that are available, alumina, silica and activated carbon, to a large extent satisfy these technical criteria and hence preferred as supports. However, alumina is by far the most widely used material.

III.1.1 Choice of Alumina As A Support.

The choice of the support invariably depends on the

TABLE III.1
Applications of Alumina In Catalysis

Application	Role of Alumina	Example
1. Alkylation	Catalyst	Phenol
2. Dehydration	Catalyst	Formic acid
3. Dehydrogenation	Carrier	Hydrocarbons
4. Isomerisation	Catalyst Carrier	1-Methyl cyclohexane Isophthalonitrile
5. Hydrogenation	Carrier	Benzene
6. Hydrodesulphurisation	Carrier	Petroleum refining
7. Hydrodenitrogenation	Carrier	Petroleum refining
8. Reforming	Carrier	Naphtha
9. Cracking	Catalyst Carrier	Hydrocarbons Naphtha
10. Hydration	Carrier	Unsaturated alcohols
11. Polymerisation	Carrier	Ethylene oxide
12. Partial oxidation	Carrier	Ethylene oxide
13. Miscellaneous		
Claus catalyst	Catalyst	Sulphur
Auto exhaust	Carrier	Platinum
Methanol synthesis	Carrier	CuO-ZnO
Water gas shift	Carrier	CuO-ZnO
Oxychlorination	Carrier	CuCl_2 -KCl

reaction to be catalysed and the reaction conditions. For acid catalysed reactions like isomerisation or alkylation, alumina is a better choice than silica because of its better and optimum acidity. The acidity of alumina can be conveniently modified

by the incorporation of suitable ions like chloride, fluoride, lithium, potassium etc (39-44). For high temperature reactions like steam reforming, dehydrogenation etc, alumina is preferred because of higher mechanical and thermal stability (46). Moreover, alumina can be prepared in a variety of crystalline forms and transition states with a wide range of surface areas and porosities suitable for different reactions, by varying the method of preparation and hydrothermal treatments (47). Alumina is used as a support for noble metals like platinum in catalytic reforming and dehydrogenation, base metals like nickel in steam reforming and benzene hydrogenation and oxides like chromium oxide in paraffin dehydrogenation (48-50).

In most of the catalyst systems studied, the role of support material is a complex one. Other than acting as a dispersant for the active species, in some cases it acts as a catalyst also. For example, in catalytic reforming on Pt/alumina, when Pt catalyses dehydrogenation, the acidic alumina catalyses cyclisation and isomerisation. The interaction of the metal with support (MSI) helps in better dispersion, stabilisation of the active species against sintering and in some systems like Co-Mo/alumina, it prevents formation of inactive species like CoMoO_4 (51). The behaviour of alumina is controlled by its structural, textural and chemical properties which in turn depend on its preparation methods. Hence the preparation of alumina has been investigated extensively.

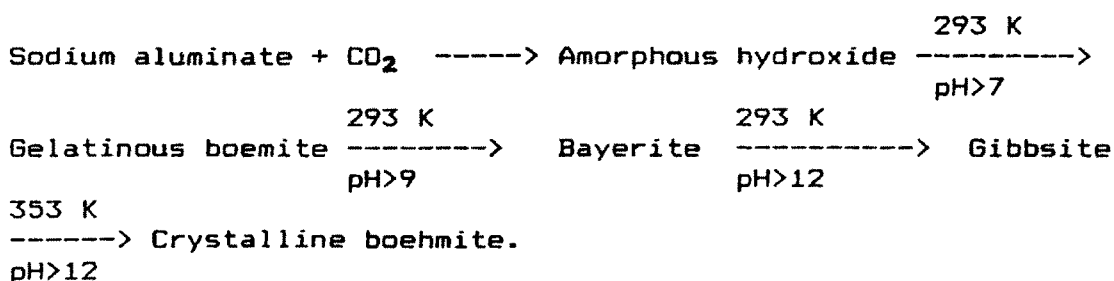
III.2 PREPARATION OF ALUMINA.

The major steps involved in the preparation of alumina

are, precipitation of aluminium hydroxide/oxyhydroxide precursor from a salt solution or a sol and calcination of the product to get various transition aluminas. A number of variables like concentration of salt solution or precipitating agent, aging time, temperature, pH, nature of atmosphere during calcination, final temperature and duration of calcination etc. influence the final properties of the resultant alumina.

1. Aluminium hydroxides and oxyhydroxides.

The two major modifications of aluminium hydroxide are trihydroxides and oxyhydroxides. Three forms of trihydroxides, α -alumina trihydrate (gibbsite), β -alumina trihydrate (bayerite) and new β - alumina trihydrate (nordstrandite) and two forms of oxyhydroxides α -alumina monohydrate (boehmite) and β -alumina monohydrate (diaspore) are the most important among the various forms reported (52). Boehmite exists in crystalline form as well as amorphous form, the latter known as pseudo boehmite. This has an X-ray diffraction pattern similar to that of crystalline boehmite, but the water content and surface area are found to be much higher. The relationship between these various forms is perhaps best illustrated by the preparation of crystalline boehmite from sodium aluminate which involves the sequence (53),



Alumina precursors can not be produced in an extremely pure

form because of the interconversions envisaged above. However, the intermediates obtained during preparations are of sufficient purity, to suit most of the catalytic purposes. Major amount of active alumina used industrially is obtained from bayerite or boehmite and hence these phases received greater attention than other phases. Identification of the various phases and their structural aspects have been discussed in detail by various authors (52,54-60). The preparation of gibbsite, bayerite and nordstrandite have been reported in the literature (52,53,62,63).

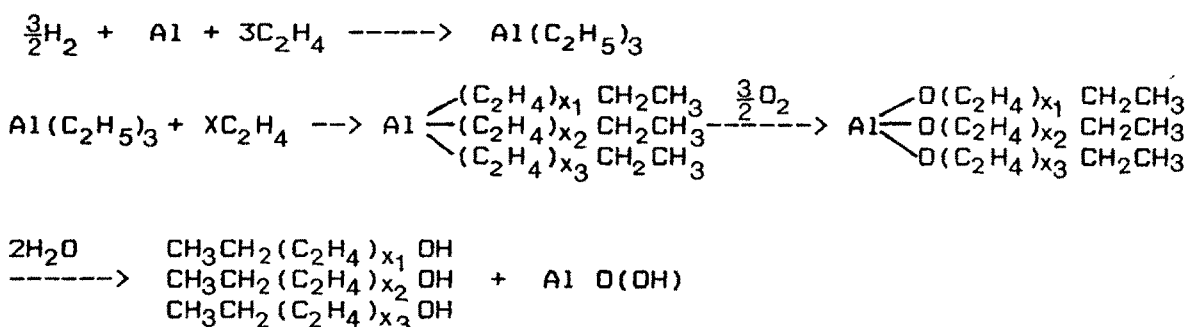
Since boehmite is the most important and useful hydroxide intermediate, its preparation will be discussed in some detail. It exists in two different forms, (1) crystalline and (2) gelatinous or pseudo boehmite. The former is the end product of aging of aluminium hydroxide gel at $\text{pH} > 12$ and 353 K (53). Gelatinous boehmite can be prepared in many ways.

i. Solutions of aluminium salts on neutralisation with ammonia yield bulky amorphous precipitates containing large amounts of water and anions which on aging in the mother liquor or in ammoniacal solutions yield pseudo boehmite (64,65).

ii. Amalgamated aluminium on oxidation with boiling water yields boehmite. If pH of water is lowered by bubbling carbon dioxide, this process can be done at room temperature (53).

iii. Solutions of basic aluminium salts on autoclaving under specific conditions of concentration, time and temperature yield boehmite in the form of uniform fibrils, 5 nm diameter and 100 nm length loosely associated into porous aggregates (66).

iv. Pseudo boehmite is manufactured on a large scale as a coproduct, utilising Ziegler chemistry in the production of linear alcohols. In this process aluminium metal is reacted with ethylene and hydrogen to form aluminium triethyl. Additional ethylene is provided to react with Aluminium triethyl and polymerise to form aluminium alkyls. These are partially oxidised to form alkoxides, which on hydrolysis give linear alcohols alongwith a slurry of aluminium hydroxide. The latter on aging under controlled pH, temperature and residence time yields pseudo boehmite (67).



Hunter and Kimberlin (68) and Kimberlin (69) describe methods for manufacturing catalyst grade alumina by alkoxide process, in which alcohols are reacted with aluminium, followed by the hydrolysis of the alkoxide.

v. A series of patents issued to Grace (70-73) describe a method of mixing sodium aluminate solution and partially hydrolysed aluminium sulfate solution containing seed crystals at a pH 7 to 8 and at a temperature 350 K to manufacture boehmite.

vi. Sanchez et al (74) used a rapid carbonation of sodium aluminate to make boehmite.

vii. Grig and Mooi(76) produced boehmite by adding a solution of urea and aluminium chloride to a hot solution of ammonium chloride.

viii. Precipitation from homogeneous solutions of Al salts utilising the hydrolysis of urea, hexamethylene tetramine or ethyl acetate also produces boehmite (76a).

ix. Another method of manufacturing boehmite spheroids which avoids the forming step (pelletisation or extrusion) is described in a patent issued to Hoekstra (77). This includes the preparation of an alumina sol from aluminium metal followed by the formation of spheres by the so called oil drop method and aging. Various modifications of the method to improve the properties of the final products have been reported in patents (78,79).

Hoekstra's procedure consists of:

- 1) Mixing of aluminium, aluminium chloride hexahydrate and water in the ratio 1:2:5.
- 2) Heating the mixture until the sol is formed.
- 3) Adding to the sol an equal volume of 30 % hexamethylene tetramine (HMTA) solution in water.
- 4) Feeding the mixture dropwise into a column (150 cm long) containing oil at about 360-370 K.
- 5) Aging of the formed spheres at 360-370 K for 16 h in oil.
- 6) Aging in ammonia solution for 16 h at 360-370 K.
- 7) Washing and drying.

The dramatic effects of aging time and temperature are shown in Hoekstra's patent. Increasing the ammonia concentration from

1.6 to 5.6% decreased the apparent bulk density (ABD) to 0.24g/ml from 0.73 g/ml of the final product. Similarly aging temperature also affects the bulk density, with higher temperature yielding the less denser product. Hayes (78) describes the method of producing eta alumina spheres by substituting HMTA with 7.84 M potassium hydroxide solution. The quality of the spheres could be improved by aging the sol-HMTA mixture below gelation temperature (79). The Al/Cl ratio in the sol affects the product density as shown in the Table III.2 (81).

TABLE NO. III.2

Effect of Al:Cl ratio on ABD.

Al/Cl ratio	ABD g/ml
0.8 : 1.0	0.75 - 0.60
1.0 : 1.2	0.60 - 0.40
1.2 : 1.5	0.40 - 0.25

It is reported that the physical strength of the spheres could be improved to the extent of 50 % by increasing the concentration of ammonia solution (0.05 - 2.5 %) with time during aging (80). Thus as described in this section, boehmite can be obtained from aluminium and its compounds in a number of ways.

2. Transition aluminas

Transition aluminas are generally prepared either by the dehydration of the trihydroxide/oxyhydroxide intermediates under well defined conditions or by the pyrolysis of aluminium salts. Route via dehydration is preferred because of the difficulties in controlling the conditions during pyrolysis. Hydroxides form a series of crystalline phases of alumina on calcination

depending on the hydrothermal conditions and phase composition of the precursors used. They are known as transition aluminas because any form can be prepared by varying the temperature of calcination, heating rate, atmosphere and particle size as shown in Figure III.1 (85)

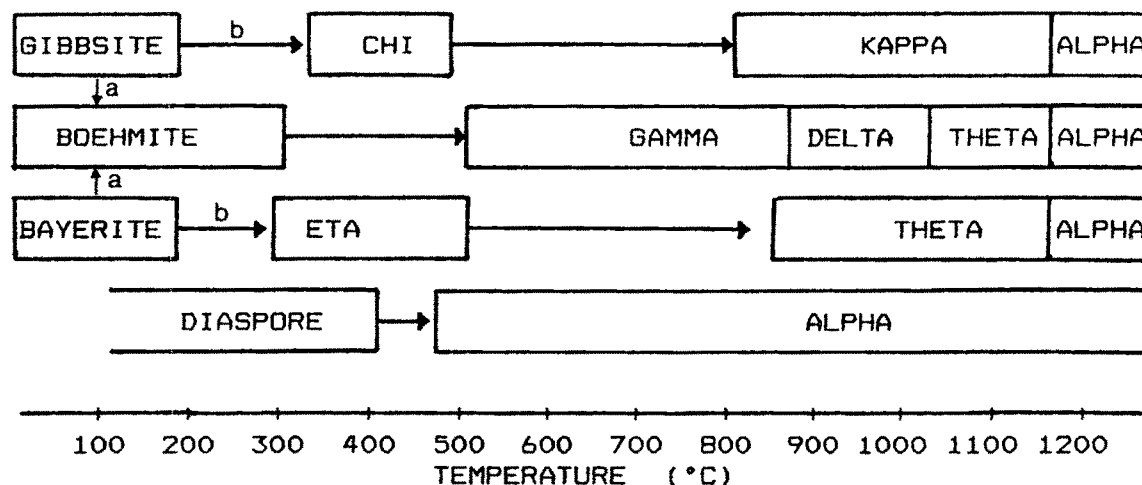


FIGURE III.1 Decomposition sequence of aluminium hydroxides.

Pathway	a	b
Pressure	>1	1
Atmosphere	Moist air	Dry air
Rate	>1	<1
Particle size	>100	<10

Among all the transition aluminas gamma and eta forms are the most important for application as supports. High surface area eta alumina is a product of dehydration of bayerite. Even though eta alumina is more active than gamma alumina, its higher acidity, lower thermal stability and higher microporosity limit its industrial use (88,89).

Pseudo boehmite is the precursor used for preparing the

frequently encountered gamma alumina than any other hydroxide. Gamma alumina has high surface area (150-300 m²/g), contains a large number of pores with diameters 3 to 12 nm and has pore volume in the range 0.5 to 1.5 ml/g. Pseudo boehmite derived delta and theta forms of alumina having surface area in the range of 100 - 150 m²/g are also used industrially in specific applications, where operations are done at temperatures too high for gamma alumina to exist or when only larger pores are desired.

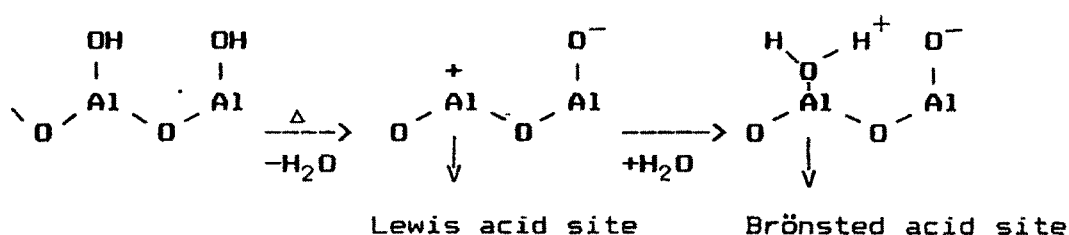
All the transition aluminas can be identified by their X-ray diffractograms. As most aluminas are poorly crystallised, the XRD lines are usually broadened. Further, the dehydration of hydroxides usually produces mixed phases (83) and hence lines overlap and identification becomes even more difficult. Although the diffraction patterns of gamma and eta phases are similar, differences exist which can still be used for their identification (84,90).

The textural properties of these aluminas vary widely and nitrogen adsorption-desorption is the best known technique to evaluate these properties. Nitrogen adsorption on aluminas have been extensively studied and reported by many authors(84,91-95).

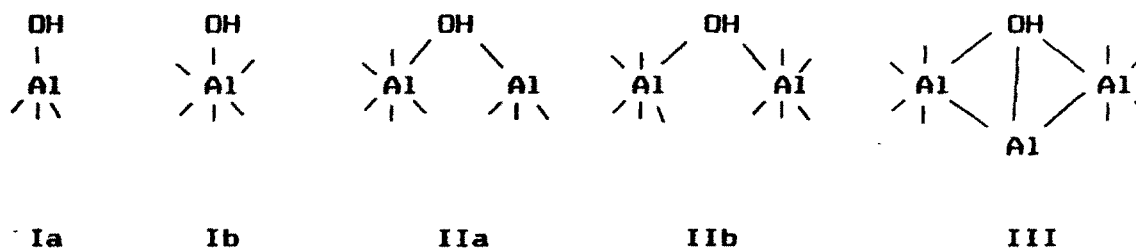
It has been demonstrated conclusively that the catalytic activity and chemisorption properties of alumina develop only after calcination at elevated temperatures in the range of 673 to 773 K. This is because active centres on the surface are generated by the removal of water/hydroxyl groups which leaves co-ordinatively unsaturated anions (oxygen ions) and cations



(exposed Al or anion vacancies) on the surface. Ordinatively unsaturated Al ions constitute the Lewis acid sites and -OH groups attached to Al atoms give rise to Brönsted acidity. The strength of the sites depends on their environments. A triple vacancy in the surface oxide layer with neighbouring high oxide ion concentration provides high degree of exposure of an aluminium ion and may constitute a strong Lewis acid site and a single vacancy may constitute a very weak Lewis acid site.



Infrared spectroscopic studies reported by Peri and Hannan (98) suggest that there could be atleast five types of -OH groups on alumina surface. This was later on modified by Knözinger and Ratnasamy (88) who gave a detailed analysis of the surface structure of various aluminas. They classify the hydroxyl groups into five types with varying strength and abundance.



Type-III is most acidic and Ia and Ib most basic. Type-III sites occur on the surface of eta alumina where (1 1 1) plane is exposed whereas in gamma alumina such sites are less abundant.

Many methods like butyl amine titration, pyridine adsorption and ammonia chemisorption can reveal information regarding acidity but ammonia chemisorption followed by temperature programmed desorption (TPD) is the most versatile, since it can provide total acidity and acid site distribution simultaneously (99).

III.3. METHODS OF MODIFICATION OF PORE STRUCTURE OF ALUMINA.

The performance of a heterogeneous catalyst is assessed in terms of activity, selectivity and life. Hence it is important to select materials having desired properties, especially the texture and stability. This necessitates the identification of the means to effectively control and modify the texture of the supports (38,46,103).

The textural characteristics are revealed in the measured values of surface area, pore volume and pore size distribution. The porosity has to be optimised so as to obtain the desired mechanical strength, since they are mutually dependent. The texture of alumina product depends on many factors like the predominant phase present and the method of its preparation.

Precipitation of any solid results in the formation of particles which agglomerate. The size and shape of particles and agglomerates affect the porosity. Large irregularly shaped particles generally give rise to bigger pores whereas small particles, because of close packing, result in decreased porosity. Small pores in alumina originate from spaces within the particles by removal of water from between the crystal planes and larger ones from interparticle spaces (52,100). A wet

atmosphere during calcination helps to maintain the particle size and as a result to increased pore size (101). Thus a normal preparation of alumina can be expected to yield a pore size distribution that depends on:

- (a) the conditions of preparation wherein hydroxide/oxyhydroxide phases are formed; and
- (b) experimental conditions during drying and calcination.

The control of pore size in alumina could be effectively done in two ways:

(1) By controlling the particle/ agglomerate size and shape.

This could be achieved by several means. Kotanigawa et al (102) have shown that precipitation with ammonia leads to a single maximum pore size at about 2 nm while precipitation with urea leads to a double maxima pore size (2.0 and 5.0 nm). Aging of precipitates after taking precautions to prevent interconversions of phases can lead to more uniform pore size distribution. Ono et al (103) suggest a method of swinging pH between acidic and alkaline during aging to prepare alumina with uniform pore size distribution. Peptisation of the precursor with suitable reagents can lead to more regular particles with a long range order because of particle bridging which in turn will give rise to uniform pore size distribution (104-107). Pyrolysis of aluminium nitrate or precipitation of sodium aluminate by carbon dioxide produces alumina with unimodal PSD whereas pyrolysis of aluminium isopropoxide and aluminium chloride lead to bimodal distribution of pores with maxima around 2 and 5 nm (102). Precipitation with ammonium bicarbonate creates

larger pores compared to pores generated on precipitation with ammonia (108).

2. By using additives.

It is established that various additives used at different stages during the preparation of alumina affect the porosity of the final product to a considerable extent. An additive may act in two different ways. An additive may possess a particular functional group which influences the pore size by reacting with aluminium hydroxides or additive may have bulky groups which cause merely physical separation of particles by the steric or space filling mechanism. Acid additives are reported to produce alumina with pores of small radii which is because of the long term order created due to peptisation. But with polycarboxylic acids the size of the group attached to the acid function is sufficient to introduce some larger pores by the space filling effect (109). Water soluble polymers like methyl cellulose ethers prevent the collapse of gel structure under the surface tension forces produced during drying and lead to larger pores. Molecular weight of such additives are reported to have negligible effect on the size of small and medium pores (109). Polyethylene oxide which is a steric stabilizer causes the attachment of the lyophobic part of the molecule to the colloid particle while the lyophilic tail trails in the solvent and stabilizes the colloid which ultimately results in a narrow pore size distribution (110,111). Low molecular weight polyethylene oxides eliminate pores of 20-100 nm size and retain 2-15 nm size pores. Increase of molecular weight causes the space filling

mechanism to become more effective and induces pores in the range of 1000 nm. Polyacrylamide causes a charge neutralisation on the hydroxide surfaces and hence flocculation of hydroxide particles. This is reported to produce a broad spectrum of pore size ranging from 5 nm to 1000 nm (109). Ammonium carbonate or bicarbonate together with other organic salts of ammonia have been tried in silica-alumina system and were found to induce pores of different size depending on the size of the groups (112,113). But tetra alkyl ammonium salts when used in similar systems were found to produce much smaller pores (114).

Moreover, during pelletisation/extrusion of alumina, fillers and binders are used routinely. Water, melamine, petroleum coke, graphite, carbon black, poly(vinyl alcohol), and grease are examples of binders. They are also reported to influence the pore structure of the calcined products (115,116).

III.4 AIM AND SCOPE OF THE WORK

The usual method of getting alumina ready for use as catalyst support is by precipitating either aluminium hydroxide or oxyhydroxide, drying, forming and calcination. The structural and textural aspects of these aluminas, as mentioned in the introductory discussion, are mainly determined by the method of preparation and hydrothermal treatments. Other than these inherent methods, the use of additives has proved to be an excellent technique to modify the texture of alumina. As is clear from the discussion given in the previous section, an additive can act in two ways: (i) Functional group effect; and (ii) Steric effect.

In the sol-gel method of spheroidal alumina preparation, the properties of the final calcined product are determined by the nature of the sol, aging conditions, and drying and calcination. The aim of the present study is to modify the properties of the calcined alumina by the use of additives, but in a somewhat different way. The alumina sol resembles a colloidal solution of aggregates of aluminium hydroxide stabilised by chloride ions. The variation in the Al/Cl ratio has a profound effect on the alumina properties which indicates the dependence of the sol structure on the anion concentration. The present work includes the use of water soluble organic acids as additives in the sol preparation stage. Once they are included in the mixture during the digestion of aluminium metal, they are expected to react with aluminium and get incorporated in the sol structure, thus modifying the properties of the sol. When other factors are maintained constant, this is expected to produce some changes in the properties of the final calcined product, like pore volume, surface area and pore size distribution. Thus various organic acids - mono and dicarboxylic, hydroxy and saturated and unsaturated - have been used at a concentration level amounting to 10% of the total chloride concentration. In order to understand the effect of these additives in the evolution of alumina phases, the hydroxide intermediates in all the cases were examined for various properties. The characteristics of the final product like crystalline state, acidity, surface area, pore volume, pore size distribution, morphology etc. have been evaluated and compared with commercial aluminas.

III.5 CHARACTERISATION OF ALUMINA SOL

The different alumina sols prepared with different acid additives were characterised for their viscosity, pH and density. Table-III.3 presents the measured values of the parameters along with the respective additives and their concentration.

The viscosities were measured at 313 K by using Ostwald viscometer and the coefficients of viscosity were evaluated in comparison with water at the same temperature. The density and pH of the sols were found to remain more or less constant irrespective of the additives. As shown in Table-III.3, the viscosity changes to a great extent as the molecular weight and nature of acid changes. In the absence of any additive the sol is expected to have a chemical composition approximately $4.5 \text{ Al}(\text{OH})_3 \text{ AlCl}_3$ as suggested by Hoekstra (77). The variations observed in viscosity evidently indicate some changes in the sol structure.

TABLE-III.3
Properties of alumina sol.

Additive	Weight of additive (g/100g Al)	pH	Density (g/ml)	Coeff. of viscosity (cp)
None (Z)	--	2.84	1.36	07.81
Acetic acid	12.50	3.20	1.36	07.81
Propionic Acid	15.42	3.10	1.36	08.06
Oxalic Acid	13.12	2.97	1.34	08.42
Malonic Acid	10.84	3.00	1.32	10.82
Succinic Acid	12.30	3.00	1.32	11.36
Maleic Acid	12.08	3.20	1.34	12.08
Citric Acid	14.58	3.00	1.36	13.38
Tartaric Acid	15.62	3.10	1.31	13.24
Adipic Acid	15.2	3.10	1.36	14.21

The other properties of the sol are listed below:

Aluminium content	wt/vol %	17.85
Chloride content	wt/vol %	13.18
Al/Cl ratio	wt/wt	1.35

The organic acids added at the sol preparation stage appear to have reacted with aluminium and got incorporated in the polymeric sol structure. A sol can be visualised as a colloidal solution of aggregates of aluminium hydroxide stabilised by chloride ions. Considerable increase in the viscosity may be due to growth of these primary colloidal particles through an interlinkage caused by the presence of the carboxylic acids containing more than one acid function. The incorporation and thus retention, of these organic moieties in the sol and gellified hydroxide were proved beyond doubt during further studies. A portion of the sample withdrawn from the furnace during calcination was found to be black which indicates the presence of partially oxidised organic acids. The DTA patterns(Fig.III.4)show strong exothermic peaks around 600 K (due to decomposition of organic moieties) indicating their retention upto the calcination stage. This can happen only if they are in the combined state, within the sol structure. Otherwise, they would have been washed away during the high temperature ammonia treatment and washing steps. Higher concentrations and higher acids were also tried, but the stability of the sols towards gellification when mixed with HMTA were so poor that they could not be used for sol-gel method of alumina preparation. This implies the formation of very large colloidal particles which are on the verge of coagulation. Even the small change of pH on mixing with HMTA, which is not

usually sufficient to precipitate the hydroxide from the sol, causes gellification in such systems, mainly due to the larger aggregate size. The changes in the morphology of the alumina samples and reduction in microporosity are also indicative of such changes in the sol structure (Table III.5).

Thus, it can be concluded that the carboxylic acids react with aluminium, get incorporated in the sol matrix and are retained till calcination stage. This causes the growth of the primary aggregates in the sol finally leading to changes in the properties of alumina.

III.6 CHARACTERISATION OF ALUMINA PRECURSORS

The alumina sols described in the previous section have been used for making spheroidal alumina by sol gel method. The formed spheres were aged in oil and then in ammonia (5 % wt/v) at 360–370 K. These spheres were then washed, filtered and dried at 423 K to get the precursors of alumina. They were characterised by X-ray powder diffraction, IR spectroscopy and thermal analysis.

III.6.1 X-ray Powder Diffraction Studies (XRD)

The X-ray powder diffractograms of some representative samples are presented in Figure III.2. All the samples prepared with and without additives showed similar patterns with sharp d-lines and were identified as boehmite, an aluminium oxyhydroxide (52). The d-lines were sharp with broadened base which reflects the presence of pseudo boehmite, known to exhibit broad and diffuse bands with d-spacings similar to the most intense bands of

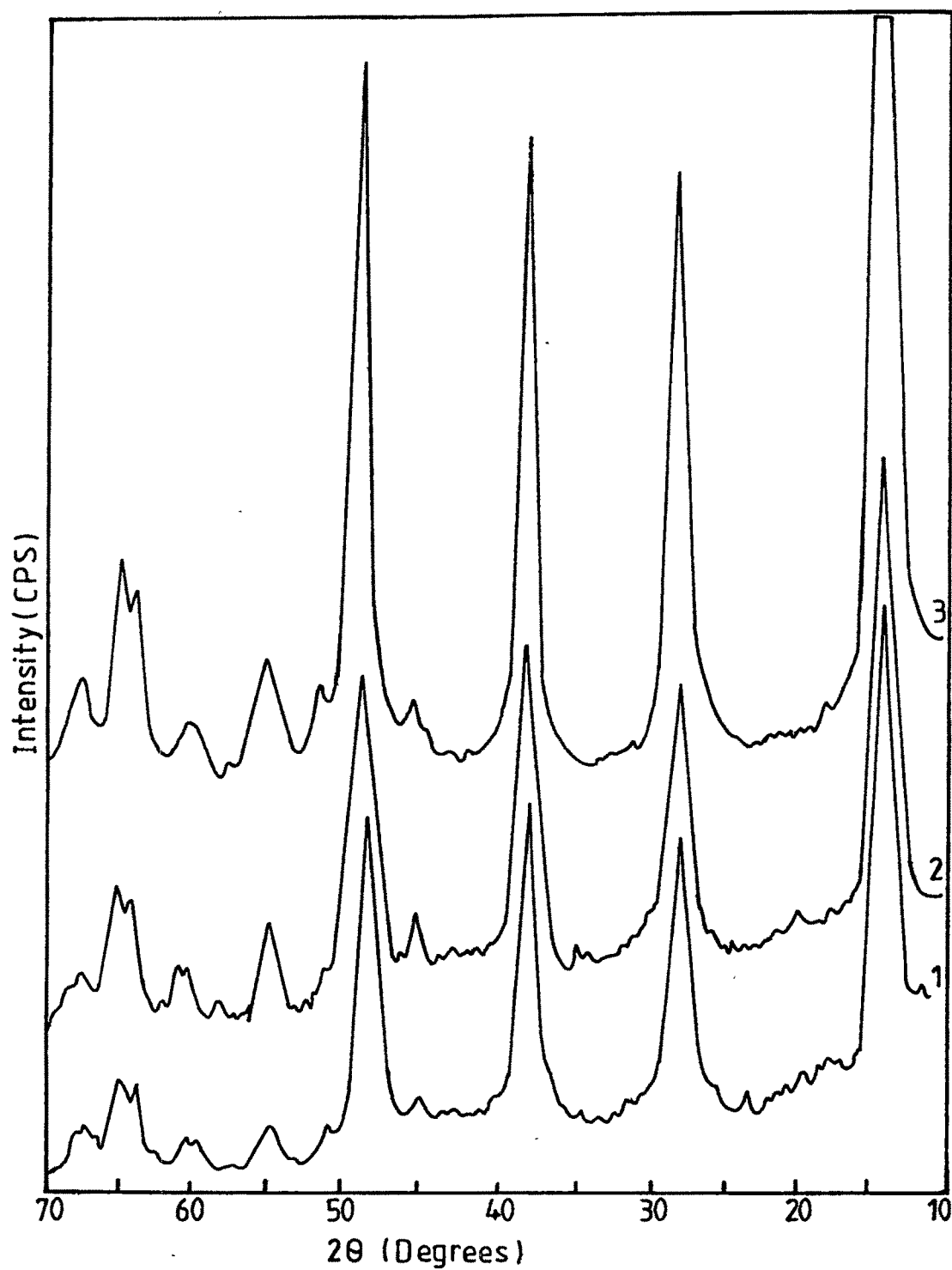


Fig.III.2 X-Ray powder diffractograms of alumina precursors.
1. Z - 423 2. Citric - 423 3. Succinic - 423.

crystalline boehmite. Small amounts of gibbsite as impurities were detected in the precursors. The peak intensities and thus percentage crystallinities were found to be different but a correlation with nature of additive could not be established.

III.6.2 Infrared Spectroscopic Studies(IR)

Different phases of aluminium trihydroxides and oxyhydroxides are reported to exhibit characteristic IR bands corresponding to stretching and bending vibrations of -OH groups (55). Broad bands at 3280 and 3080 cm^{-1} correspond to -OH stretching vibrations of boehmite. The -OH bending vibrations of boehmite are observed at 1150 and 1070 cm^{-1} . A peak at 1620 cm^{-1} appears in samples with and without additives which is attributed to the adsorbed water molecules.

IR spectra of a few samples are depicted in Fig. III.3. For higher acids like citric and tartaric acids, band appear at 1350-1440 cm^{-1} which may be due to -C-O-H bending. This peak is found to be absent in samples with lower acids and that without additive. The IR data reconfirms the fact that, the formed phase is mostly boehmite only.

III.6.3 Thermal Analysis.

Differential thermal analysis results of the alumina precursors are presented in this section. If the alumina precursors are different from each other, they will vary widely in crystal structure, degree of hydration and crystallinity. Hence, they will behave differently when subjected to a thermal treatment (85). The DTA patterns of some precursors which showed

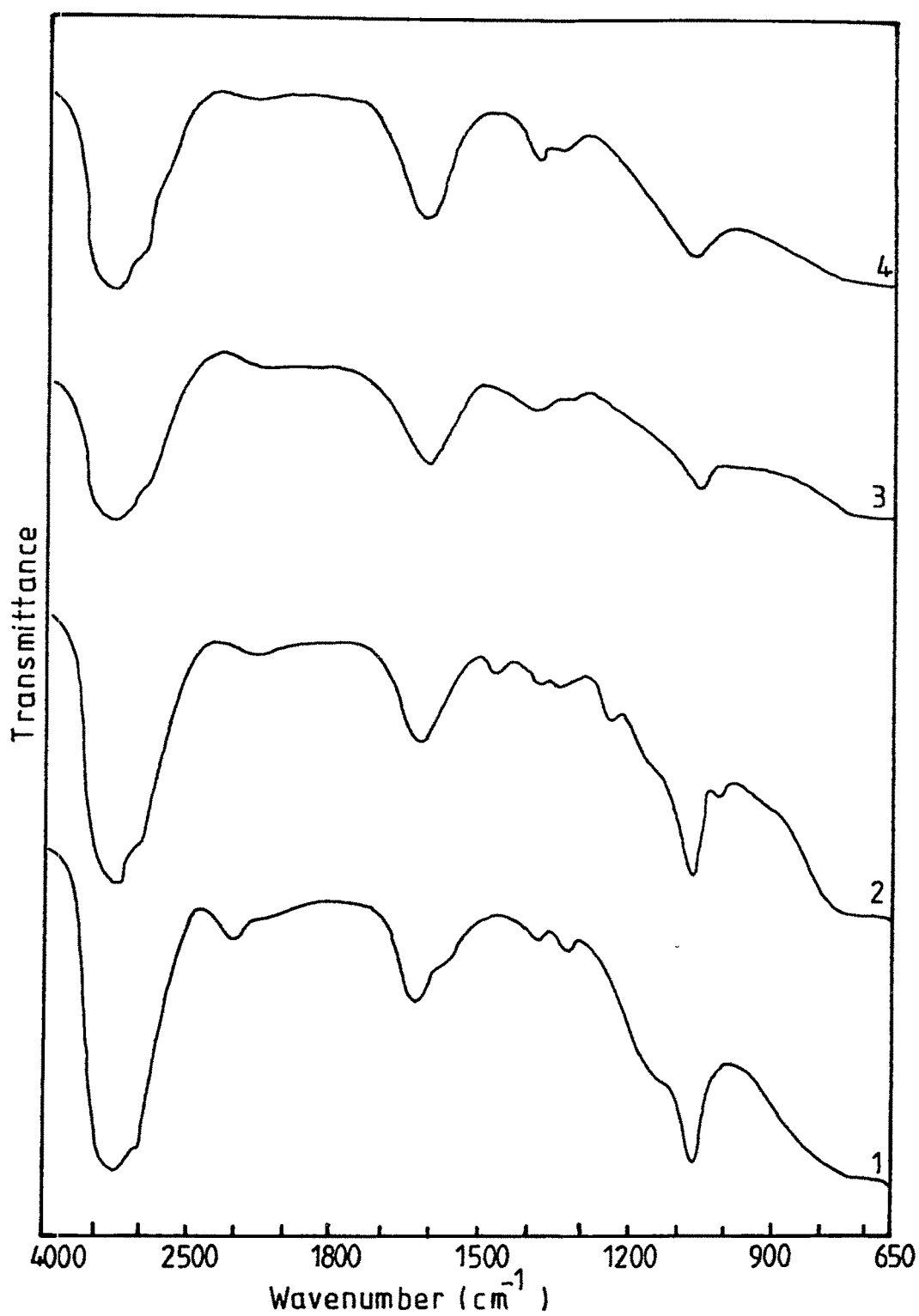


Fig.III.3. Infrared spectra of alumina precursors
1. Z-423 2 Succinic-423 3 Citric -423
4. Tartaric - 423

distinct features are depicted in Figure III.4. Curve 1 in the figure is the DTA pattern of alumina precursor prepared without any organic acid. It exhibits three endothermic maxima at 510, 591 and 731 K. The peak at 510 K could be due to the dehydration of a trihydroxide impurity and the one at 591 K due to the dehydration of pseudo boehmite. The third endothermic maximum at 731 K can be attributed to the dehydration of crystalline boehmite to gamma alumina (85). After 773 K the curve shows a continuous endothermic shift probably due to the slow transition to alpha alumina. Curve 2, that of Acetic-423 is similar but shows a small exothermic shoulder at 645 K which could be due to the decomposition and oxidation of the organic moiety. Curves for Propionic-423, Oxalic-423 and Malonic-423 were also very much similar with the exothermic peak becoming more and more intense. Curve 3 is the DTA of Succinic-423 which shows two endothermic maxima at 533 and 731 K and one intense exothermic peak at 600 K. The endothermic peak at 731 K corresponds to the dehydration of boehmite to gamma alumina and the one at 600 K (exothermic) is attributed to the oxidation of succinate group. The curves for Adipic-423, Citric-423 and Tartaric-423 also are similar except for the fact that the exothermic maximum is at 653 K and gamma transition around 713-723 K. The appearance of the exothermic peak in the above described systems clearly shows the presence of reacted carboxylic acid moieties strongly bound to the hydroxide frame work.

The situation existing during this mode of preparation, is somewhat unique in nature. During the prilling operation, the

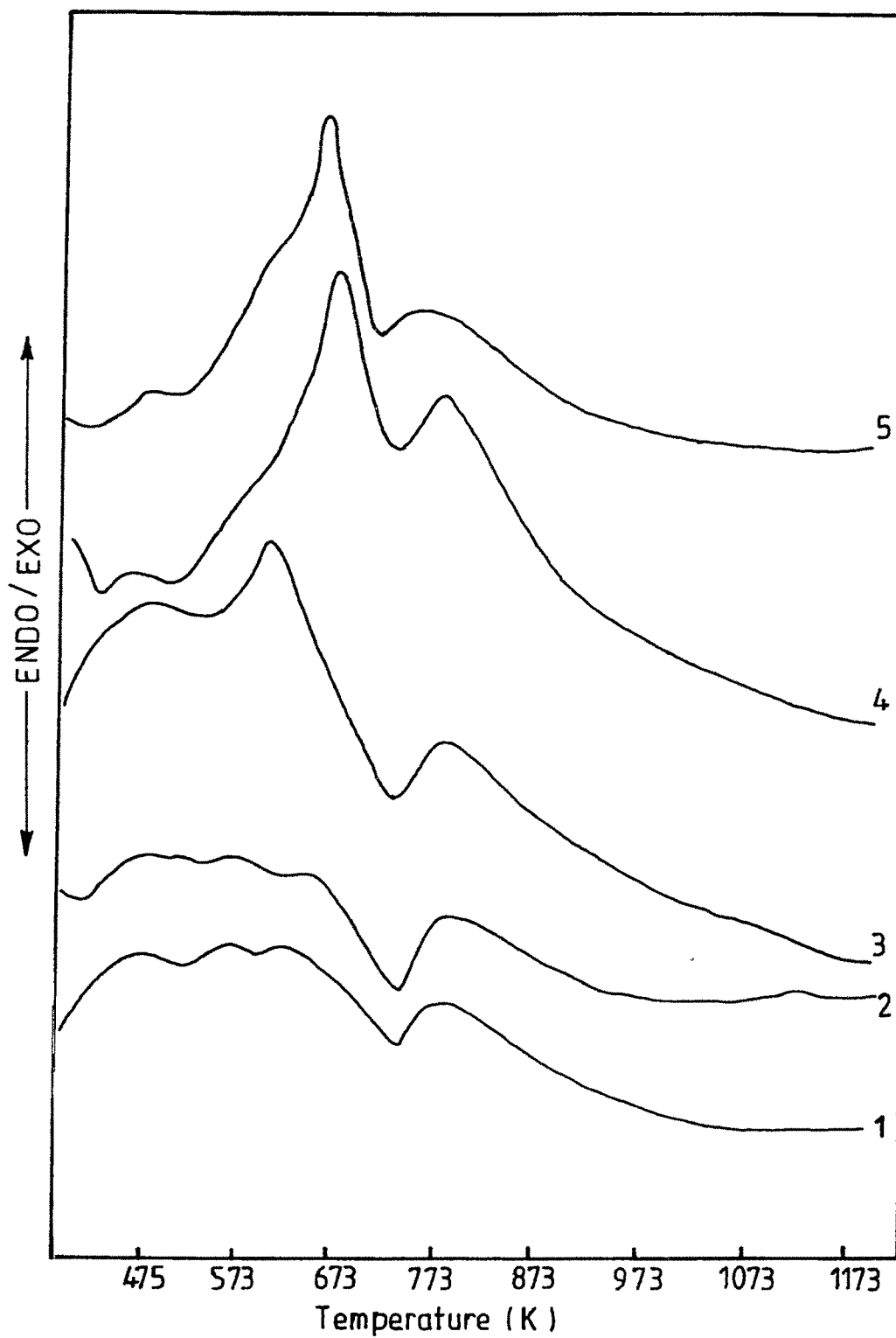


Fig.III. 4. DTA Patterns of alumina precursors.

- | | | |
|-----------------|-------------------|-----------------|
| 1. Z-423 | 2. Acetic-423 | 3. Succinic-423 |
| 4. Citric - 423 | 5. Tartaric - 423 | |

drops of Sol-HMTA mixture are fed into the oil column kept at 368 K. The pH of the drop changes from about 4 to 10 within one or two seconds. The solid formed at the gellification point may be amorphous hydroxide which slowly gets converted into primarily crystalline boehmite on aging under the prevailing conditions of $\text{pH} > 10$ and temperature 368 K (53). But the hydrothermal conditions inside the individual spheres may be slightly different and may lead to other forms of hydroxide impurities. Thus, it can be concluded that the nature of the precipitating agent and the temperature of aging are the determining factors for the formation of a particular phase.

III.7 CHARACTERISATION OF TRANSITION ALUMINAS

All the alumina precursors prepared and characterised as described in the previous sections were calcined at 823 K for 3 h to obtain the transition aluminas. They were characterised by average sphere size, apparent bulk density, X-ray diffraction, scanning electron microscopy, nitrogen adsorption and desorption studies, ammonia chemisorption and temperature programmed desorption of ammonia. One commercial alumina (CK-300) was also characterised for comparison.

III.7.1 Average Sphere Size.

Eventhough the orifice size used in all the preparations was the same, the average sphere size of the calcined products showed minor variations. Propionic-823, Citric-823 and Malonic-823 exhibited a shrinking effect while Oxalic-823, Succinic-823 and Adipic-823 showed a small expansion of the sphere. The size of the spheroids varied from 1.34 to 1.91 mm

as shown in Table III.4.

TABLE III.4

Physical and chemical properties of alumina samples.

Sample	Average size (mm)	ABD (g/ml)	Crushing strength (Kg)	Acidity (moles NH ₃ /g/m ²) × 10 ⁶
Z-823	1.70	0.31	0.95	2.4
Acetic-823	1.76	0.32	1.28	2.3
Propionic-823	1.34	0.37	fragile	4.0
Oxalic-823	1.96	0.26	0.34	2.7
Malonic-823	1.38	0.76	4.04	3.4
Succinic-823	1.88	0.38	1.82	2.2
Maleic-823	1.67	0.44	1.39	3.1
Citric-823	1.59	0.63	4.21	2.0
Tartaric-823	1.75	0.50	3.46	2.4
Adipic-823	1.91	0.51	2.98	2.0

III.7.2 Apparent Bulk Density (ABD)

ABD of all the samples were determined and are found to vary from 0.26 to 0.76 g/ml. The data are presented in Table III.4.

III.7.3 Crushing Strength (C.S.)

The mechanical strength of the products are expressed as the amount of pressure a particle can withstand before crumbling. Alumina without additive exhibited a C.S. of about 1 Kg and the values for all other samples were found to be higher than this except for Oxalic-823. Citric-823 and Malonic-823 exhibited abnormally high values in the order of 4 Kg but the ABD values of these samples were also correspondingly high. Again a correlation of the mechanical strength with nature of the additive could not be established as can be seen from Table III.4.

III.7.4 X-ray Diffraction Studies (XRD)

Figures III.5,6 and 7 present the XRD patterns of

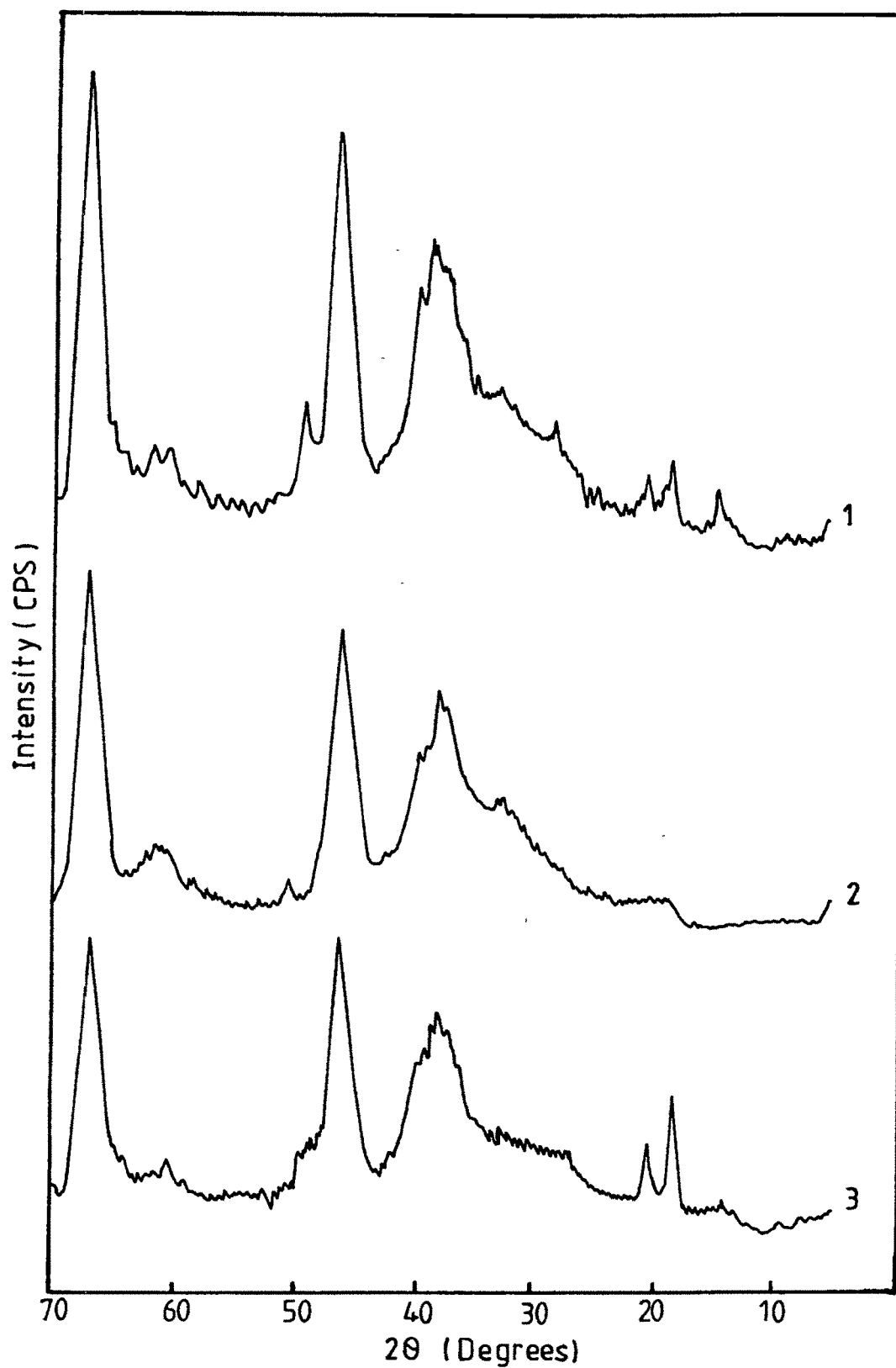


Fig.III. 5. X-Ray powder diffractograms of alumina samples
1. Z-823 , 2. CK-300 , 3. Tartaric -823

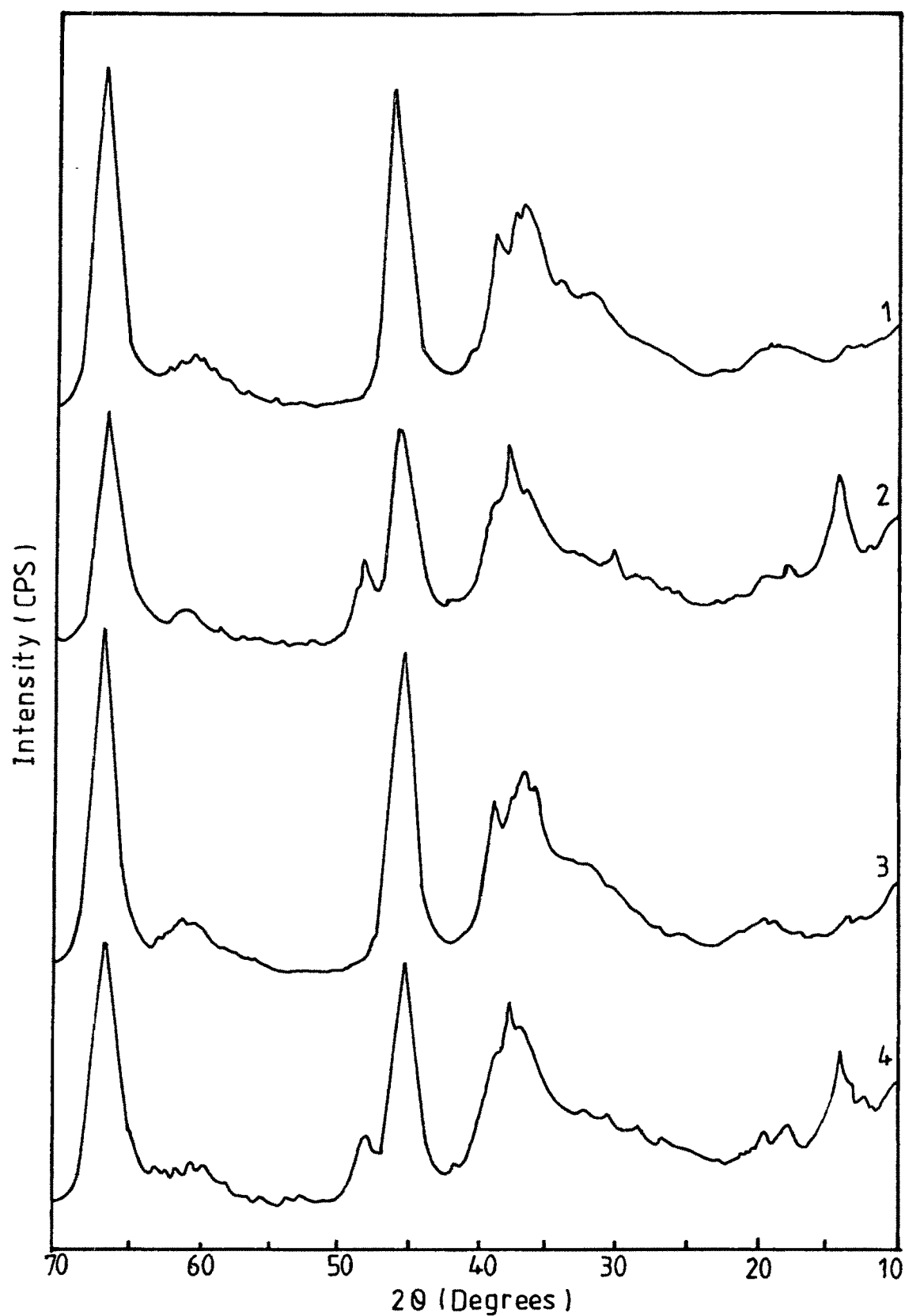


Fig.III.6. X-Ray powder diffractograms of alumina samples

1. Acetic-823 , 2. Propionic-823 , 3. Oxalic-823 , 4. Malonic- 823

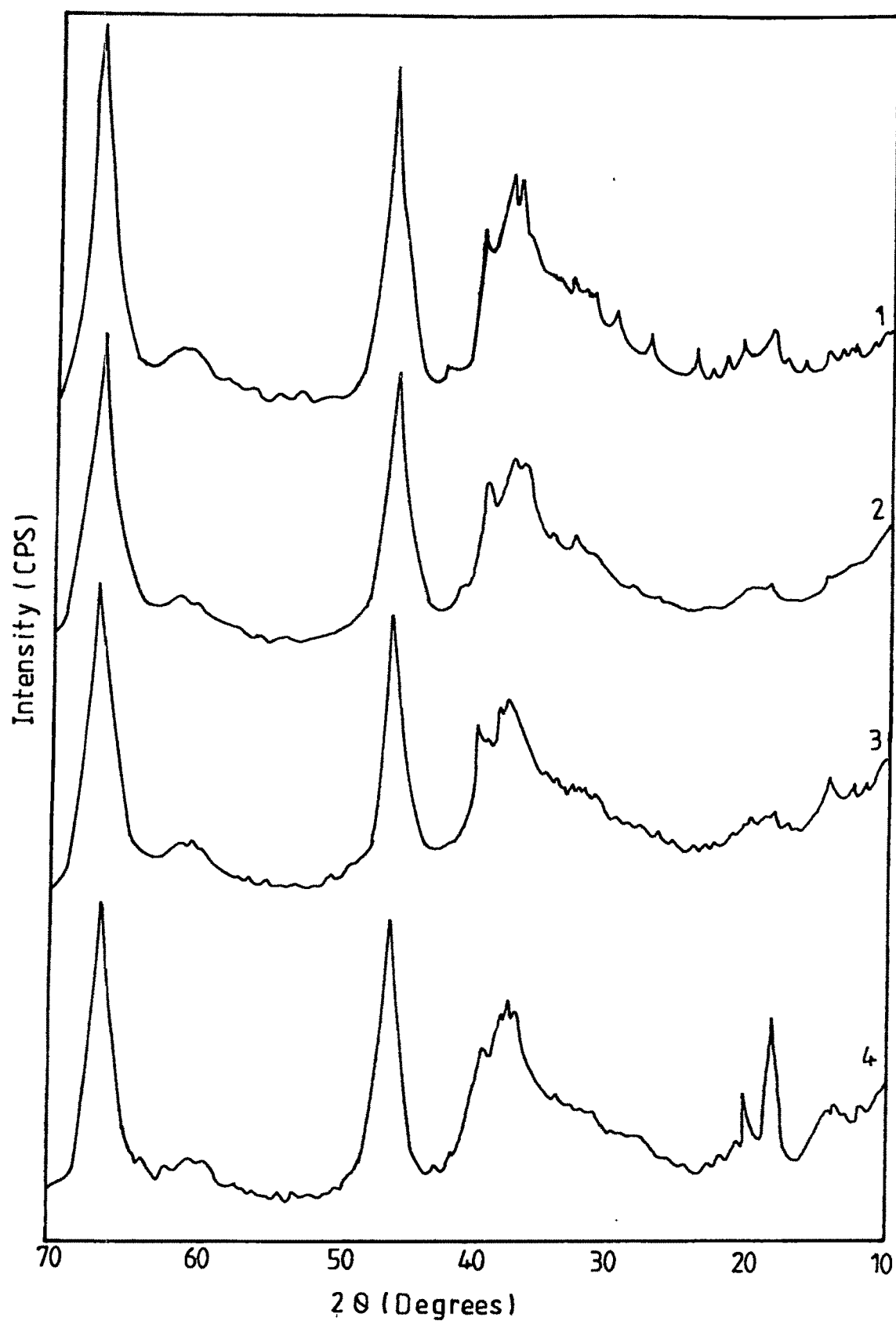


Fig. III.7. X-Ray powder diffractograms of alumina samples
1. Succinic-823, 2. Maleic-823, 3. Citric-823, 4. Adipic-823

transition aluminas. Since the precursors were mostly boehmite and proper calcination procedures have been adopted to avoid formation of any undesired phase, the expected phase was only gamma alumina. The XRD patterns were diffuse and broad exhibiting d-spacings characteristic of either Eta or Gamma alumina. The formation of eta phase is unlikely because the precursors did not contain any bayerite modification. The distinction between gamma and eta phases even though difficult because of close similarity, could be made on the basis of two differences.

- (i) The 1.98 \AA° band is doubled in the case of gamma alumina where as eta phase exhibit only an assymetric profile.
- (ii) The 4.6 \AA° band of gamma alumina is very broad while that of eta is sharp with a broadened base (73,103).

Most of the XRD patterns of the samples exhibit unclear doubling of 1.98 \AA° band and some cases the peak shows a plateau. In all the cases 4.6 \AA° band is present which is found to be very broad. Hence, it can be concluded that the major phase present is gamma modification. Malonic-823 and Propionic-823 show additonal peaks at 6.12 and 1.86 \AA° indicating the presence of traces of boehmite (52). Similarly, diffractograms of Tartaric-823 and Adipic-823 show bands at 4.8 \AA° and 4.35 \AA° corresponding to gibbsite impurities (52). The XRD pattern of CK-300 does not show any band other than that of gamma alumina and it can be inferred that it does not contain appreciable amounts of other phases. Since the history of its preparation is unknown, it is not possible to derive any further conclusions

regarding the phases present.

III.7.5 Morphology of Alumina Samples

Scanning electron micrographs of the samples taken at 3000 and 10000 magnifications are presented in Plates III.1, 2 and 3. Without any added acid component, the alumina particles appear as small agglomerates of irregularly shaped particles with fairly wide distribution of size. Addition of acetic and propionic acids to the sol matrix results in the formation of larger agglomerates alongwith irregularly shaped platelets. Addition of oxalic or succinic acid brings out small and yet irregularly shaped particles of varying size. In presence of malonic acid, however, the morphology is entirely different, and consists of small needle shaped particles with relatively narrow size distribution. Modification with an unsaturated dibasic acid (maleic acid) results in particles of varying size and shape and larger average particle size. The two hydroxy acids, citric and tartaric, lead to the formation of different and mutually distinguishable morphology. Citric acid modification results in alumina with large and approximately spherical agglomerates, consisting of needle shaped small, fine particles of uniform size. This structure is indicative of relatively higher proportion of macropores. Tartaric acid gives alumina particles with the shape of molten glass beads with narrow size distribution.

The inference that could be drawn from the morphological study of alumina samples is that addition of acids and their incorporation in the sol matrix definitely change the size and shape of primary particles. The extent of agglomeration is

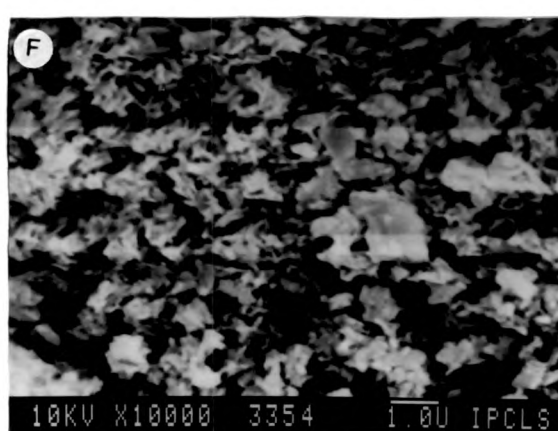
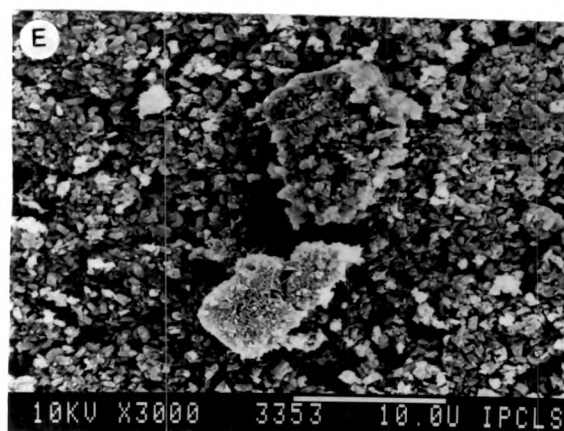
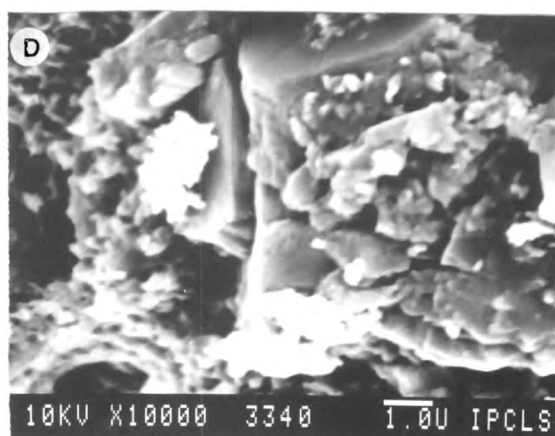
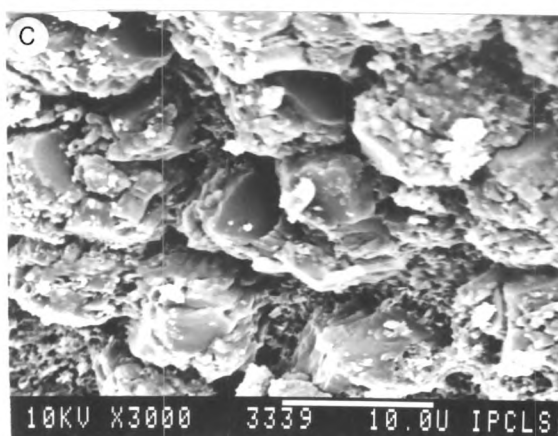
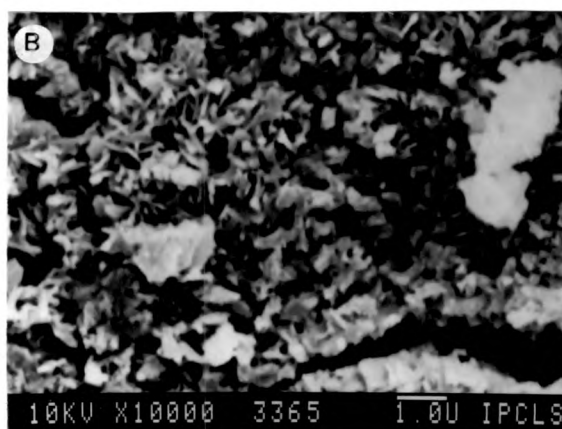
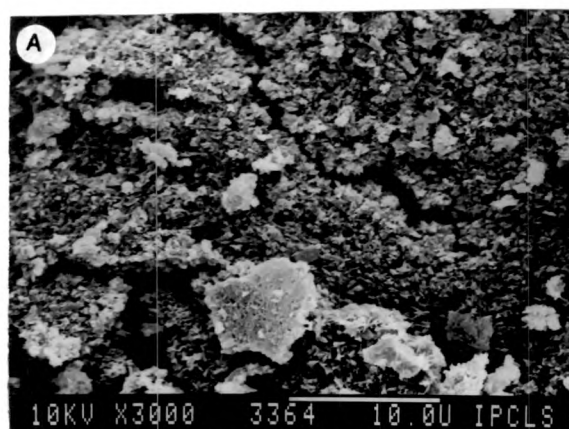


PLATE III.1 SCANNING ELECTRON MICROGRAPHS OF ALUMINA SAMPLES

(A),(B) Z-823 (C),(D) Acetic-823 (E),(F) Oxalic-823

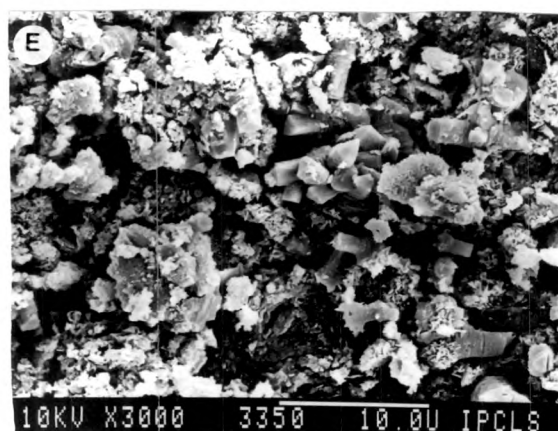
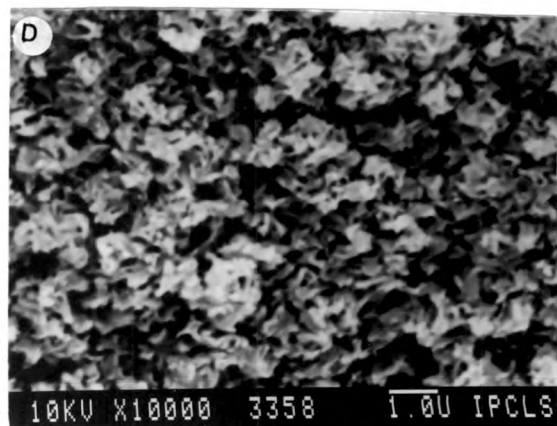
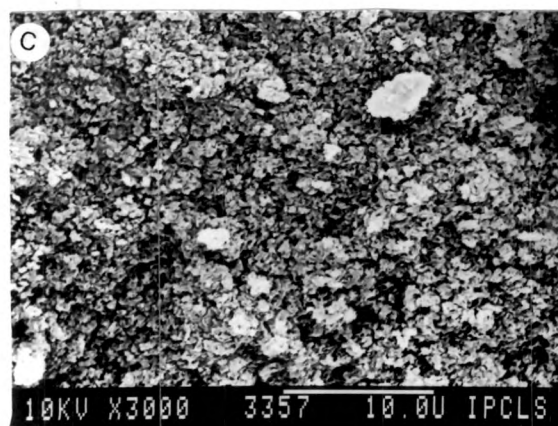
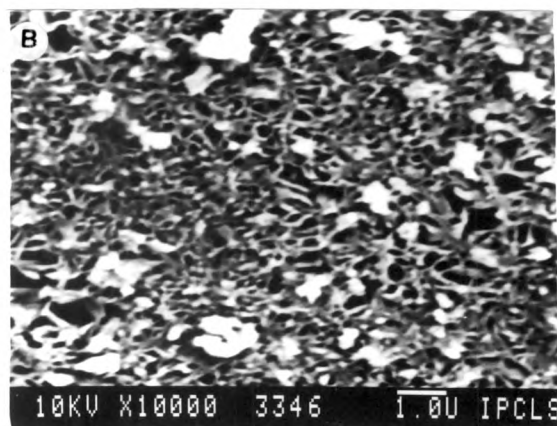
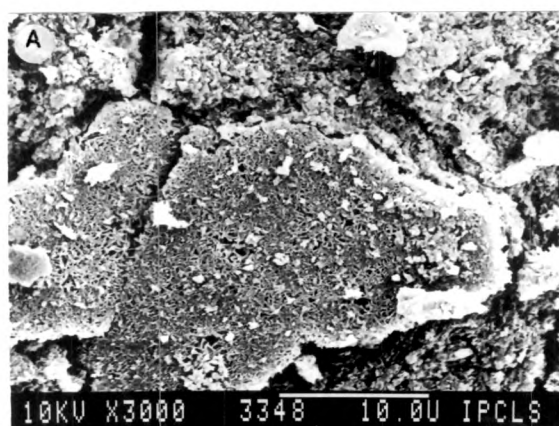


PLATE III.2 SCANNING ELECTRON MICROGRAPHS OF ALUMINA SAMPLES

(A),(B) Malonic-823 (C),(D) Succinic-823 (E),(F) Maleic-823

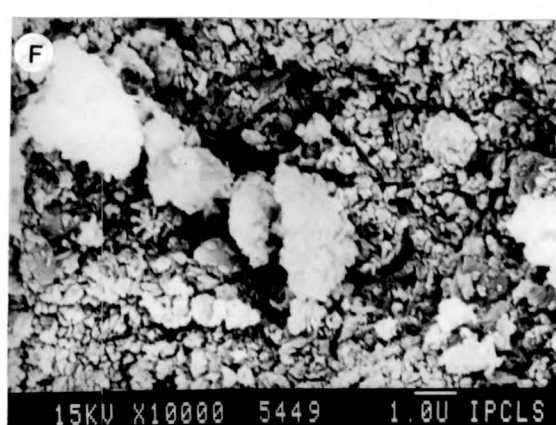
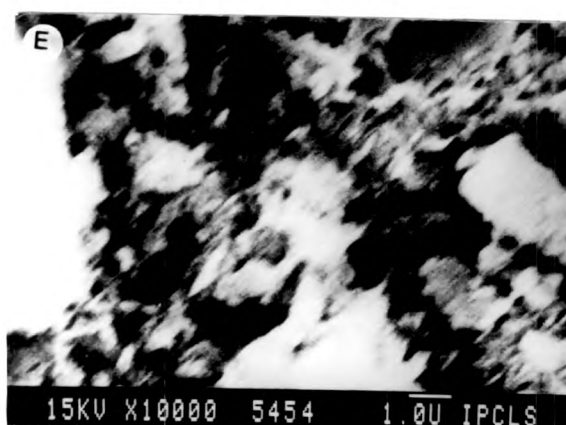
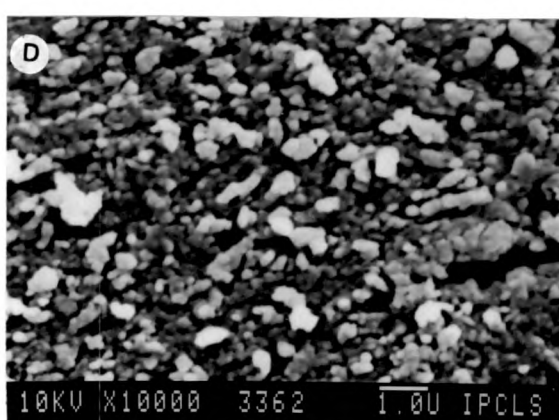
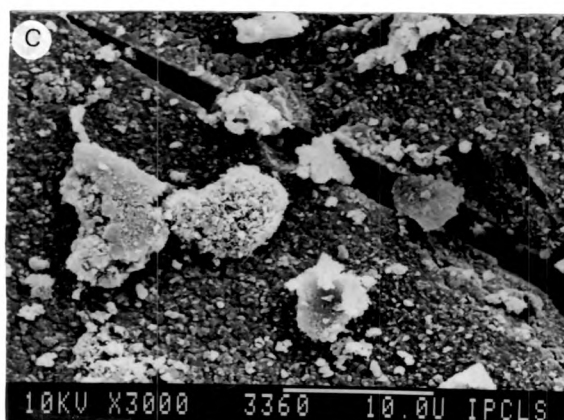
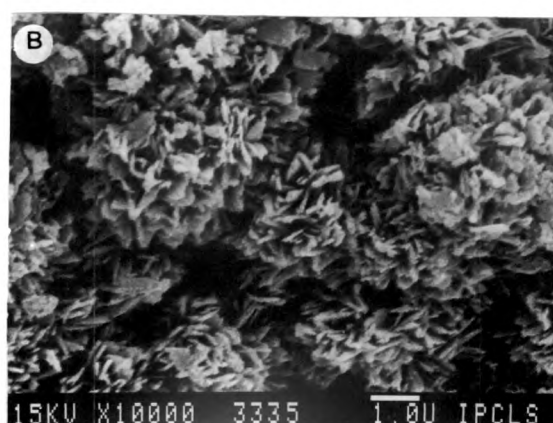
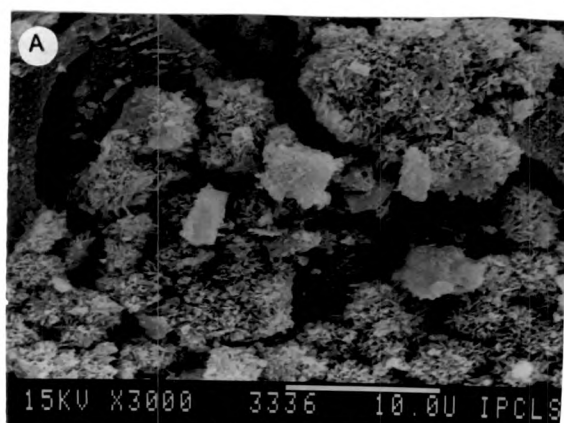


PLATE III.3 SCANNING ELECTRON MICROGRAPHS OF ALUMINA SAMPLES
 (A),(B) Citric-823 (C),(D) Tartaric-823 (E) Propionic-823
 (F) Adipic-823

dependent on the kind of the acid used. However, no definite correlation between the nature of the acid and the morphology could be observed. The observed differences in the morphology clearly show that the acid moities have entered the sol matrix and control the size of the colloidal particles of aluminium hydroxychloride. The calcination of these primary particles result in the formation of alumina particles with distinct morphology and crystallites of varying size.

III.7.6 Textural Properties.

The textural characteristics of alumina include: crystalline state, average size of basic particles and porosity. X-ray diffraction studies already discussed in Section III.7.4 have revealed that the major phase existing is gamma modification. Moreover, the packing density and hence porosity are determined by the size and shape of the primary crystallites and agglomerates. SEM results show the presence of particles of varying size and shape. Further studies by X-ray Line Broadening Analysis (XLBA) to determine the average crystallite size (217) show that (Table III.5) the sizes are not much different from each other and are in the range of 52-62 Å. But invariably the crystallite sizes of the modified samples are equal to or less than that of Z-823 except for Maleic-823. The extent of crystallinity of the samples were also determined by comparing the intensities of the most intense d-lines of gamma phase with those of standards having known crystallinity. The percentage gamma crystallinity were found to vary from 51-66 with a maximum shown by Maleic-823. (Table III.5)

The surface area and porosity of alumina samples were analysed with the help of shape of adsorption - desorption isotherms of nitrogen, volume adsorbed versus thickness of multi-layer curves, hysteresis loops and evaluation of pore size distribution by BJH method (118). The results of the study are presented in Table.III.5.

The shape of the adsorption isotherms for all the samples appear to be a combination of Types IV and V isotherms as per the classification of Brunauer et al (221), indicating that in general all the alumina samples studied are essentially mesoporous in nature. The type of Va-t curves shown in Figures III.11,12,13 reveal that both cylindrical micropores and slit shaped meso and macro pores are present in the alumina samples (95,119).

TABLE III.5
Textural Properties of Alumina Samples

Sample code	Specific surface area (m ² /g)	Pore vol. (ml)	Mean pore radius (Å)	Pore size distribution (%)			Average crystallite size (Å)	Gamma crystallinity (%)
				micro <20Å	meso 20-500Å	macro >500Å		
Z-823	170	0.61	72	26.35	66.07	7.58	59	58
Acetic-823	134	0.45	67	17.84	71.66	10.50	56	61
Propionic-823	98	0.40	81	12.26	77.74	10.00	53	44
Oxalic-823	147	0.44	60	20.82	69.25	9.93	56	63
Malonic-823	121	0.48	79	12.34	77.88	9.78	56	49
Succinic-823	134	0.55	82	9.99	72.03	17.99	62	66
Maleic-823	136	0.52	76	12.74	87.26	0.00	59	54
Citric-823	134	0.67	100	9.90	76.61	13.49	56	55
Tartaric-823	145	0.66	91	13.40	80.21	6.38	54	51
Adipic-823	157	0.55	70	14.90	67.86	17.24	58	56

The shapes of hysteresis loops for the samples depicted in Figure III.8,9,10 do not correspond to any one of the five types of standard/ideal shapes presented in the literature. According to the classification by de Boer (120) there are five types of hysteresis loops corresponding to different sizes and shapes of pores. All the samples exhibit reversible part in the isotherm at low relative pressures and hysteresis loop at higher relative pressures. However, the shapes of the hysteresis loops observed for alumina samples could be easily approximated to a combination of Types A & B indicating the presence of slit shaped pores alongwith cylindrical pores (121). This observation apparently coincides with the conclusion drawn from the analysis of V_a-t curves and the shape of adsorption isotherms.

The classification of pores into micro, meso, and macropores, as presented in Table III.5, is also in agreement with the conclusion arrived at on the basis of the shape of the adsorption isotherm. The results show that 66-87 % of the pores are in the meso size range.

It is observed from the above discussed results that, the addition of organic acids to alumina sol matrix alters the pore size distribution to a considerable extent (Table III.5). In general, the addition of acid brings down the micropores content in the alumina and increases the meso and macro pores content. The extent of variation in pore size distribution is related to the acid used, though no definite correlation could be seen with respect to their nature/type. The decrease in the content of micropores, decreases the surface area as expected, and

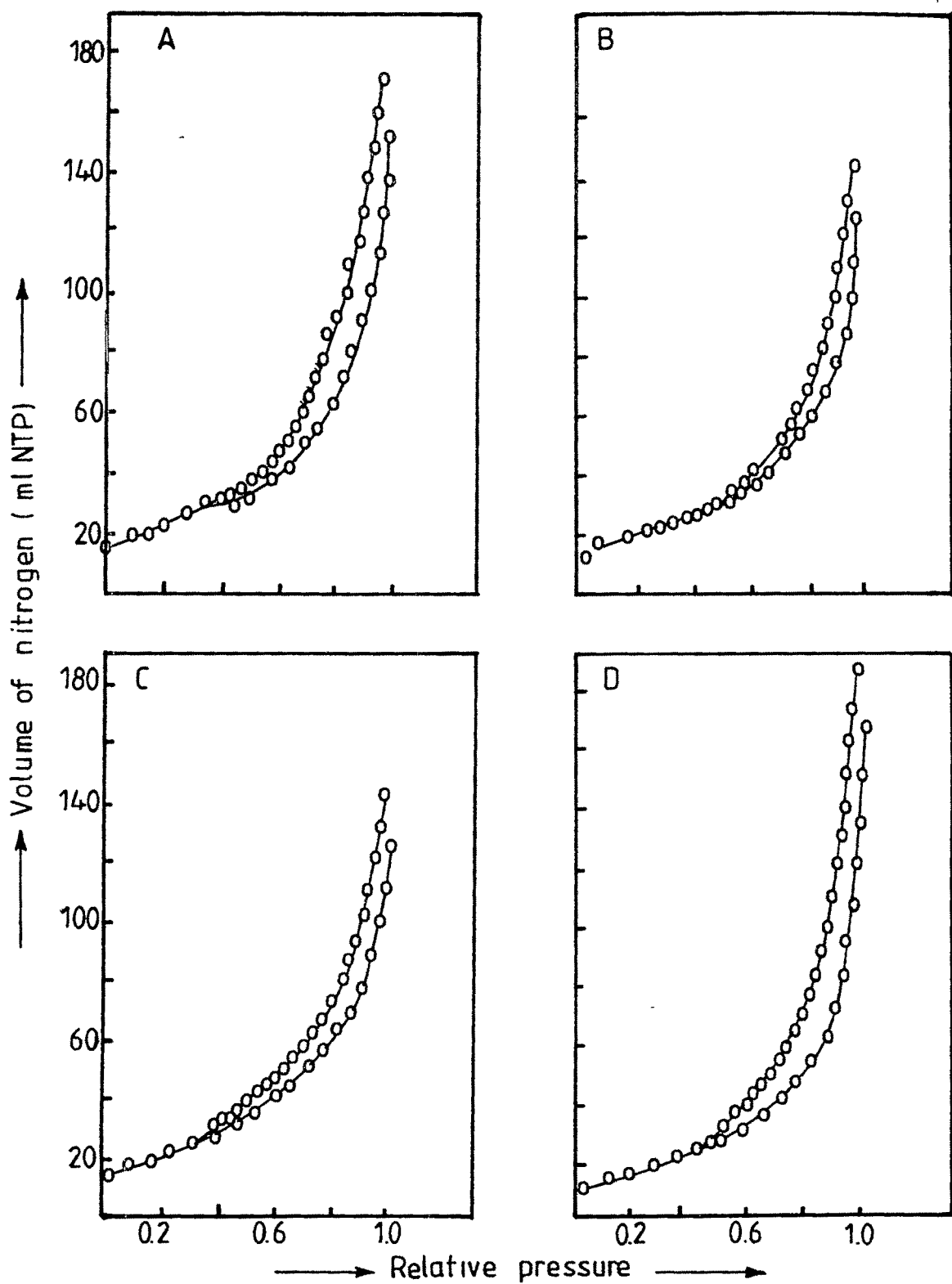


Fig.III.8. Adsorption-Desorption Isotherms of N_2 on alumina samples
 A. Z-823, B. Acetic-823, C. Oxalic-823, D. Succinic-823.

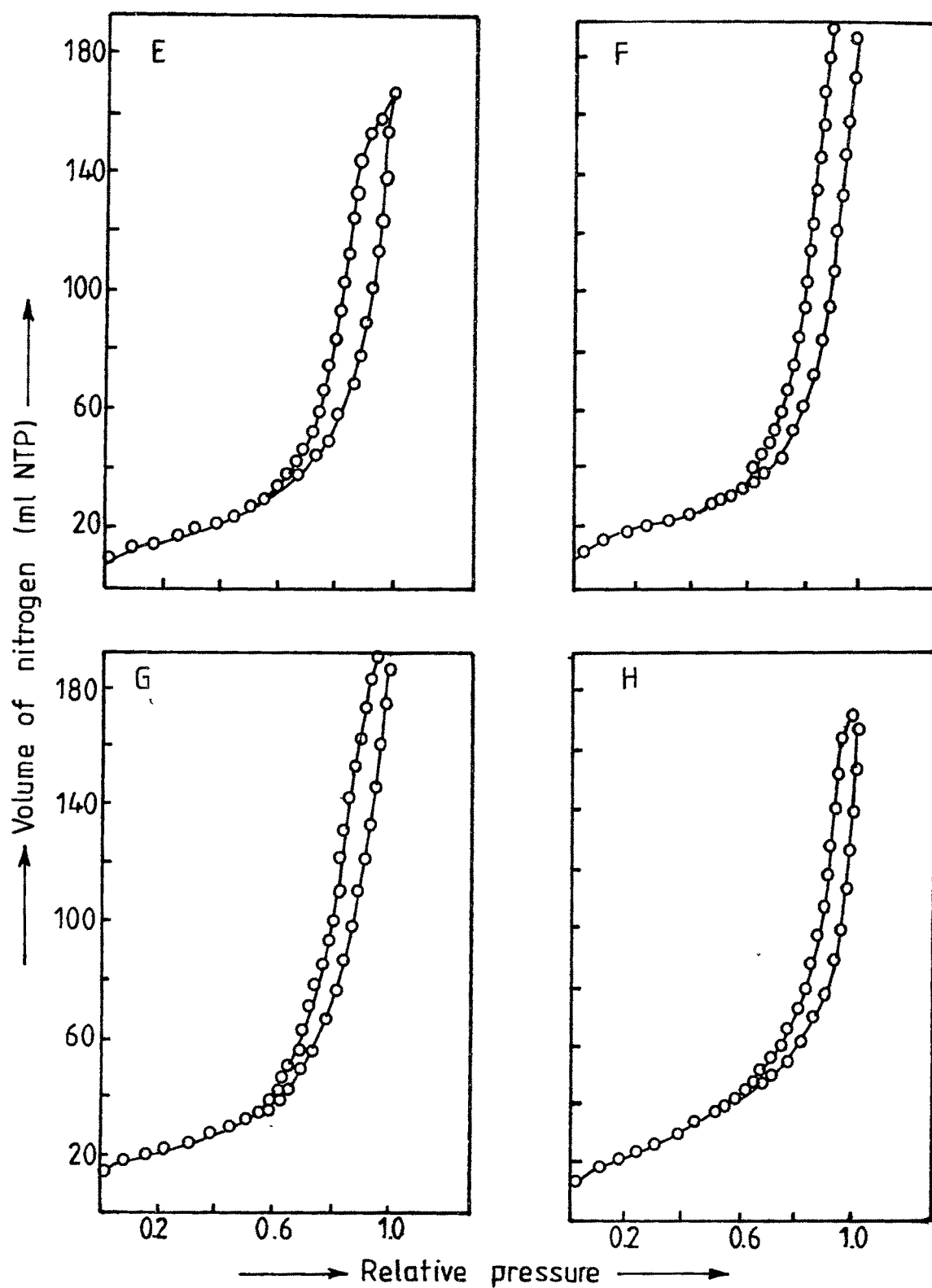


Fig. III.9. Adsorption - Desorption Isotherms of N_2 on alumina samples
 E. Malonic-823 , F. Citric- 823 , G. Tartaric-823, 4. Adipic-823.

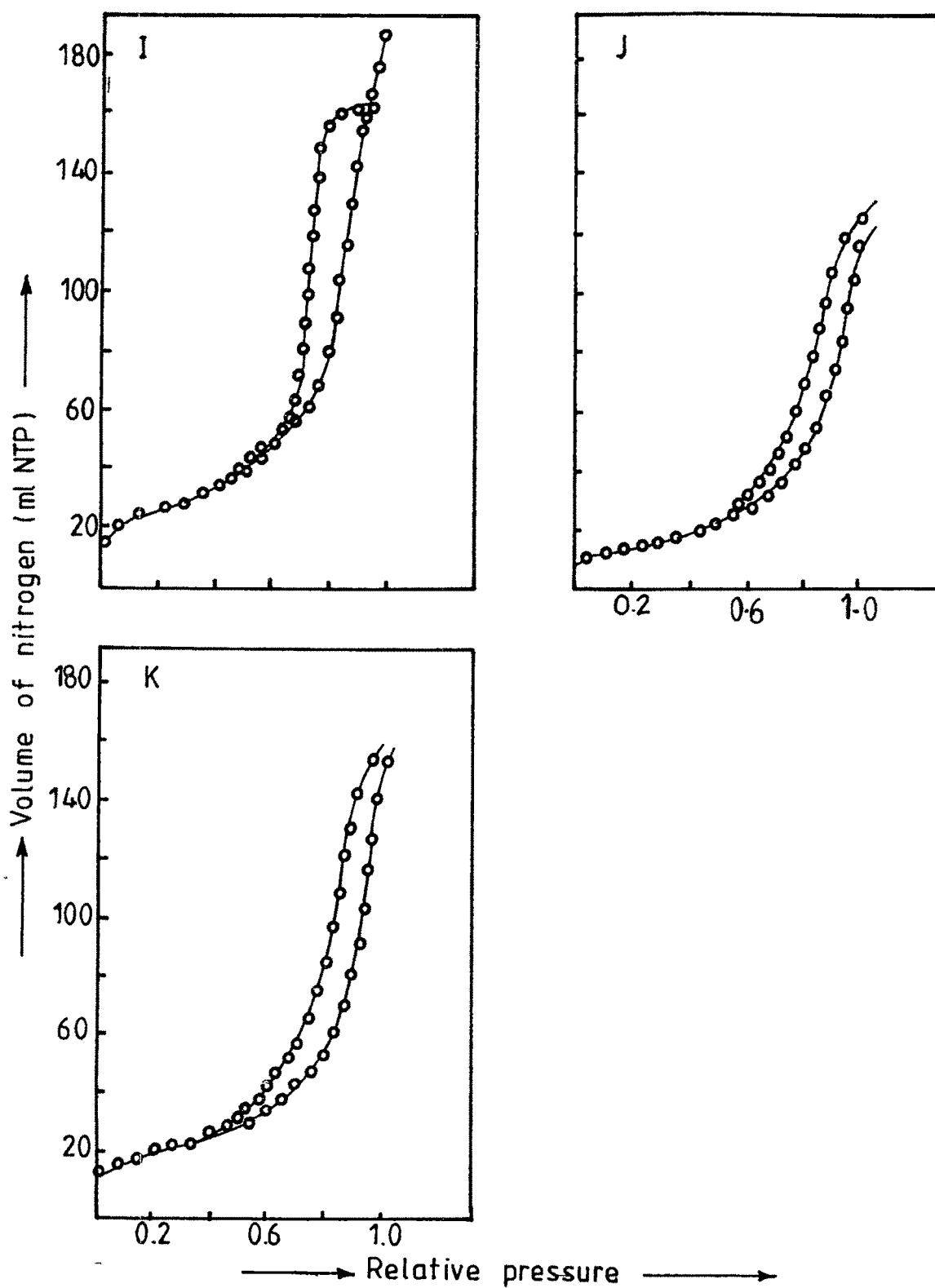


Fig. III.10. Adsorption-Desorption Isotherms of N_2 on alumina samples
I. CK-300, J. Propionic-823, K. Maleic-823.

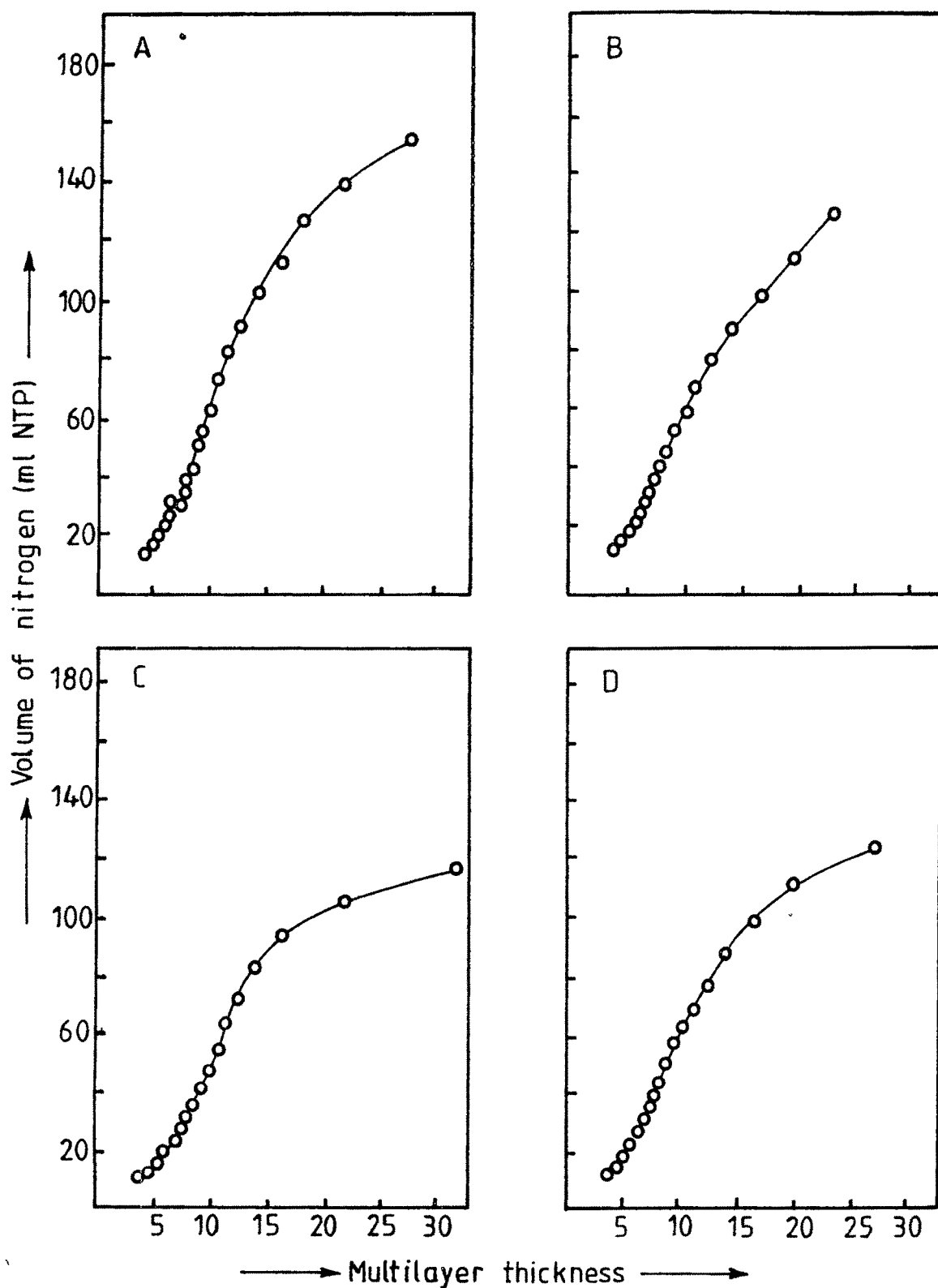


Fig.III.11 Va-t curves of alumina samples
 A. Z-823 , B. Acetic-823 , C. Propionic-823 , D. Oxalic-823.

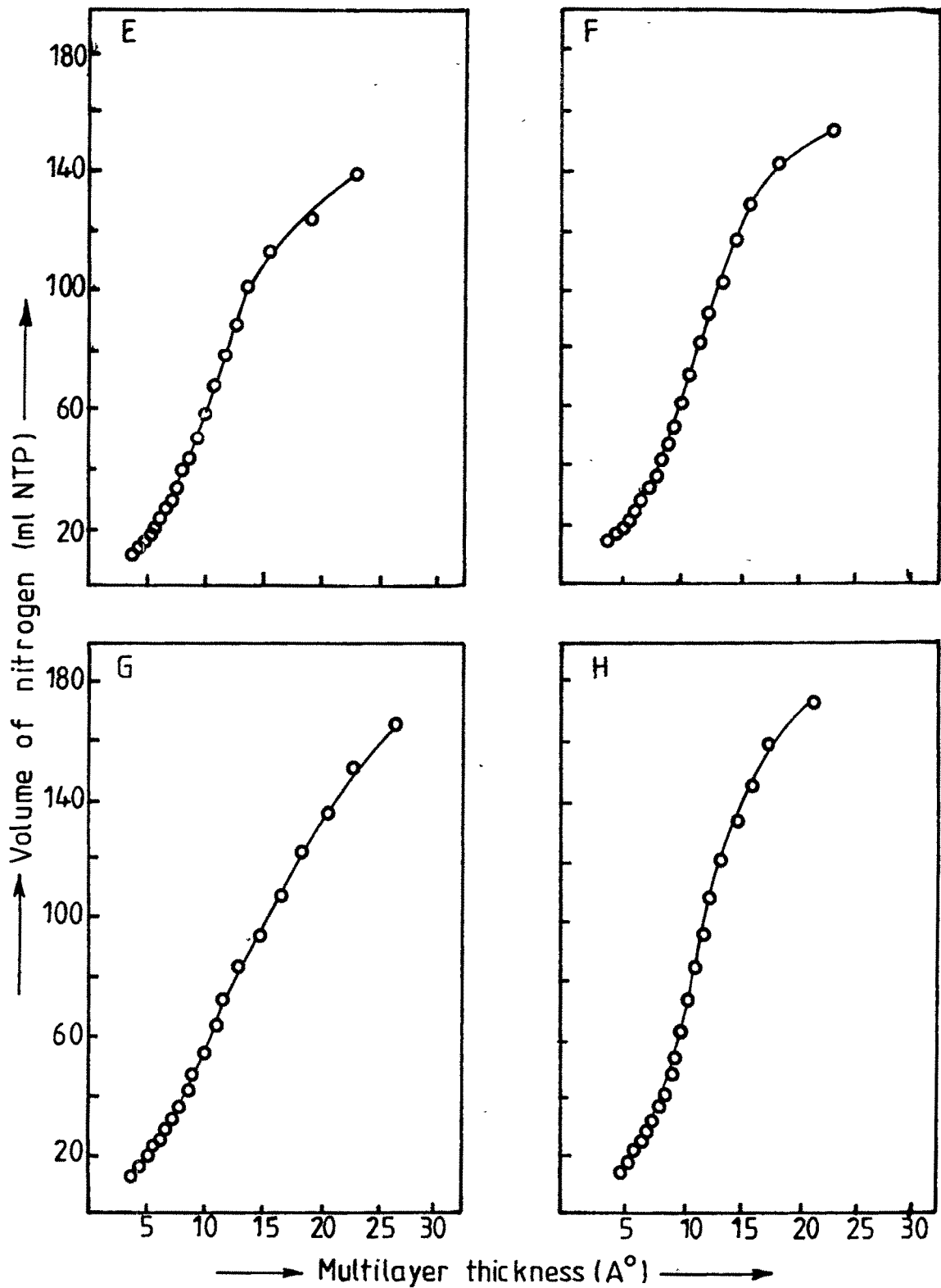


Fig.III.12 Va-t curves of alumina samples
 E. Malonic-823 , F. Maleic-823 , G. Succinic-823 ,
 H. Citric - 823 .

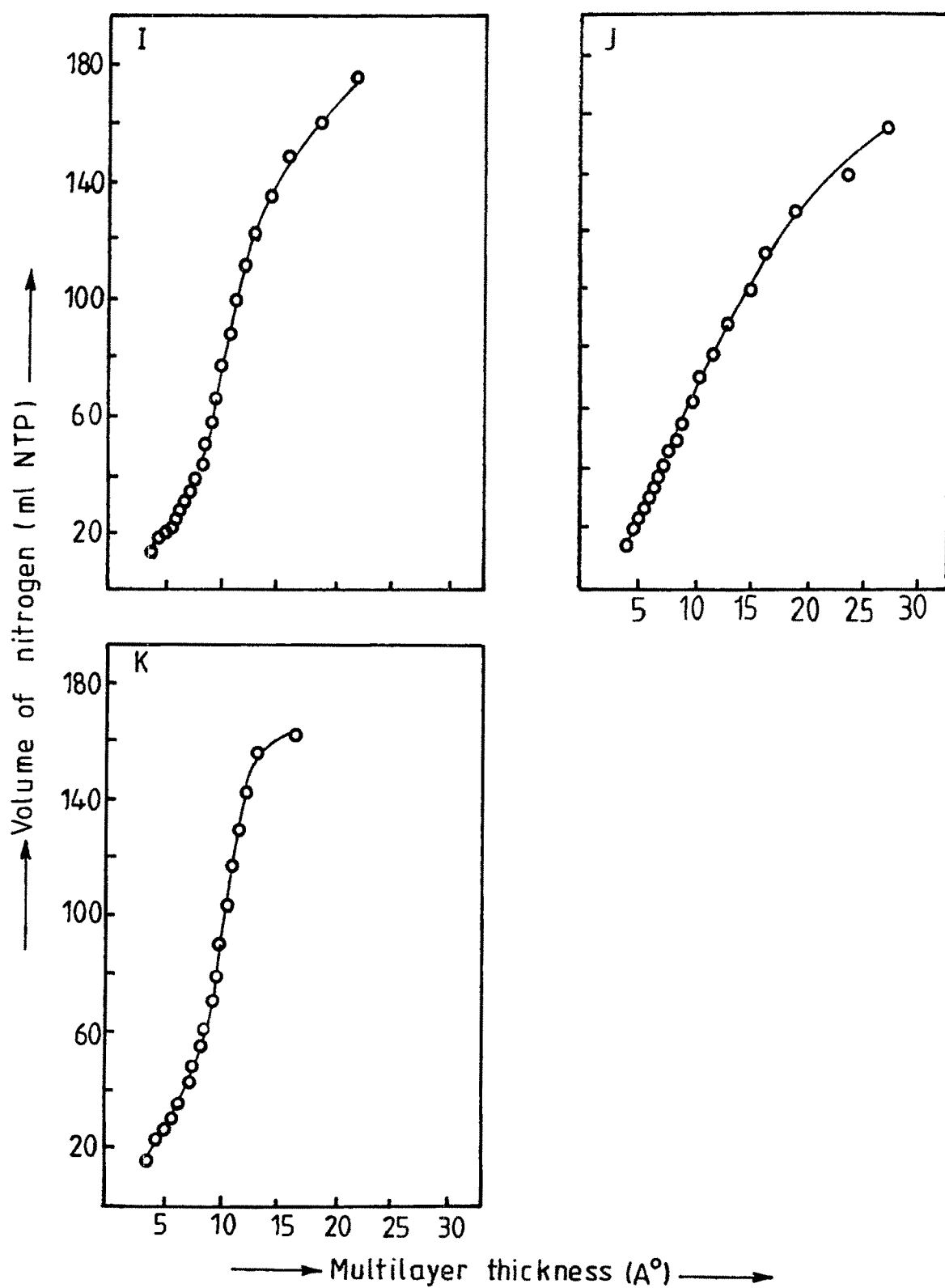


Fig.III.13 Va-t curves of alumina samples

I. Tartaric-823 , J. Adipic-823 , K. CK-300

correspondingly, the pore volume and mean pore radius also, as shown in Table III.5.

The lowest value for surface area and pore volume was observed for alumina sample obtained by the addition of propionic acid. As seen in Table III.5 the size of the spheres obtained with propionic acid is the smallest, indicating perhaps the formation of very fine particles, that are packed in a compact manner. This arrangement probably reduces the pore volume as well as the surface area. A closely related observation is the variation of average crystallite size for various alumina samples. The formation of primary particles and their density of packing which are governed by the acid additives thus alter the ultimate pore structure.

The pore size distribution curves as presented in Figures III. 14,15 and 16 clearly bring out the variation in pore structure as different acids are added to the alumina sol structure. A gradual increase in meso and macro pores, with a concurrent decrease in micro pores is distinctly seen. While Acetic-823, Oxalic-823, Malonic-823 and Succinic-823 essentially maintain the bimodal pore structure, the hydroxy acids Citric and Tartaric result in nearly monomodal (meso type) pore structure.

III.7.7 Surface Acidity Measurements.

The surface acidity measurements were carried out by ammonia chemisorption and TPD. The experimental set up and procedure for the dynamic pulse method are detailed in Chap.II. 4.8. The total acidity of the samples calculated as moles

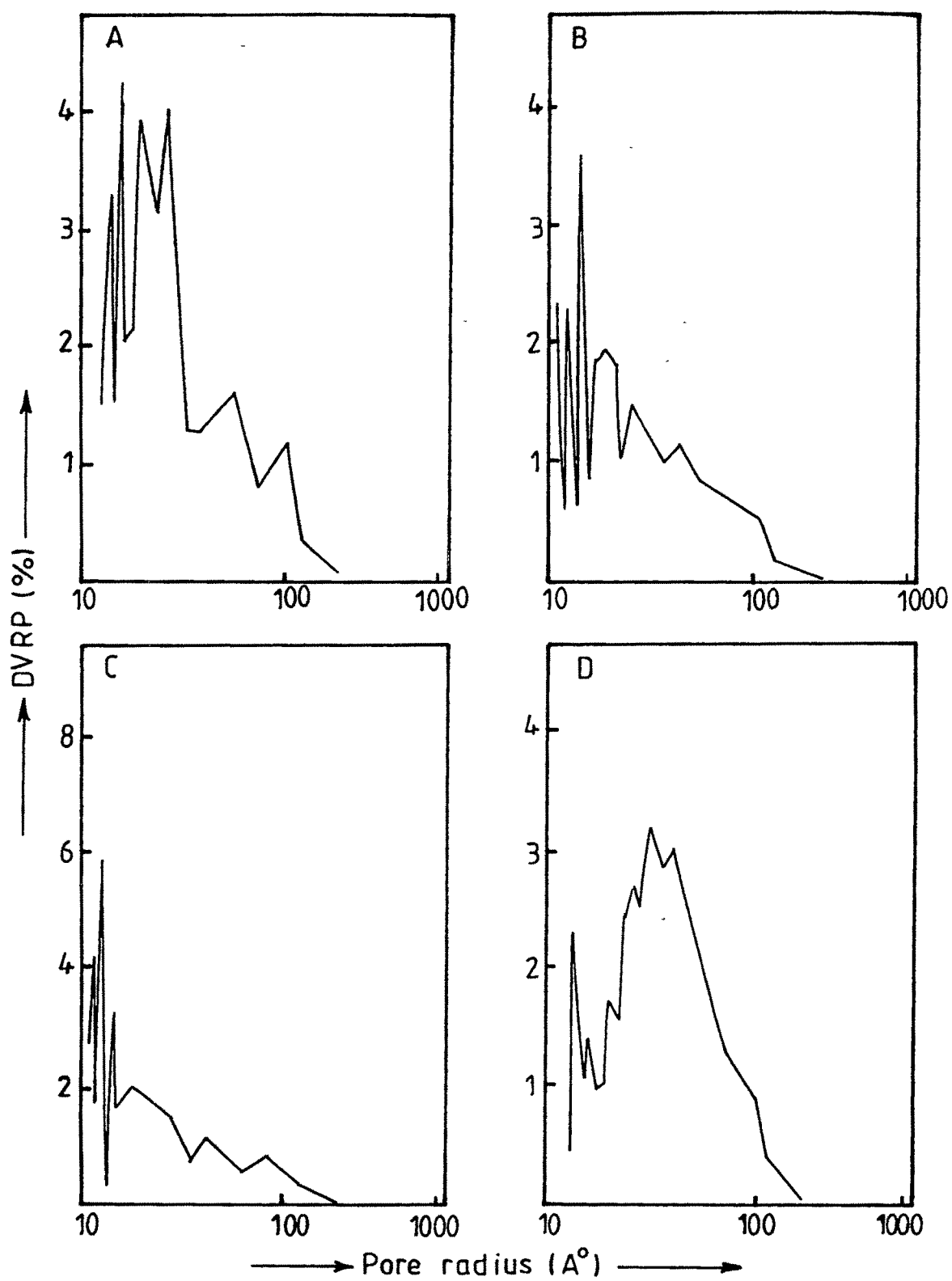


Fig. III.14 Pore size distribution curves of alumina samples.

A. Z-823, B. Acetic-823, C. Oxalic-823, D. Malonic-823

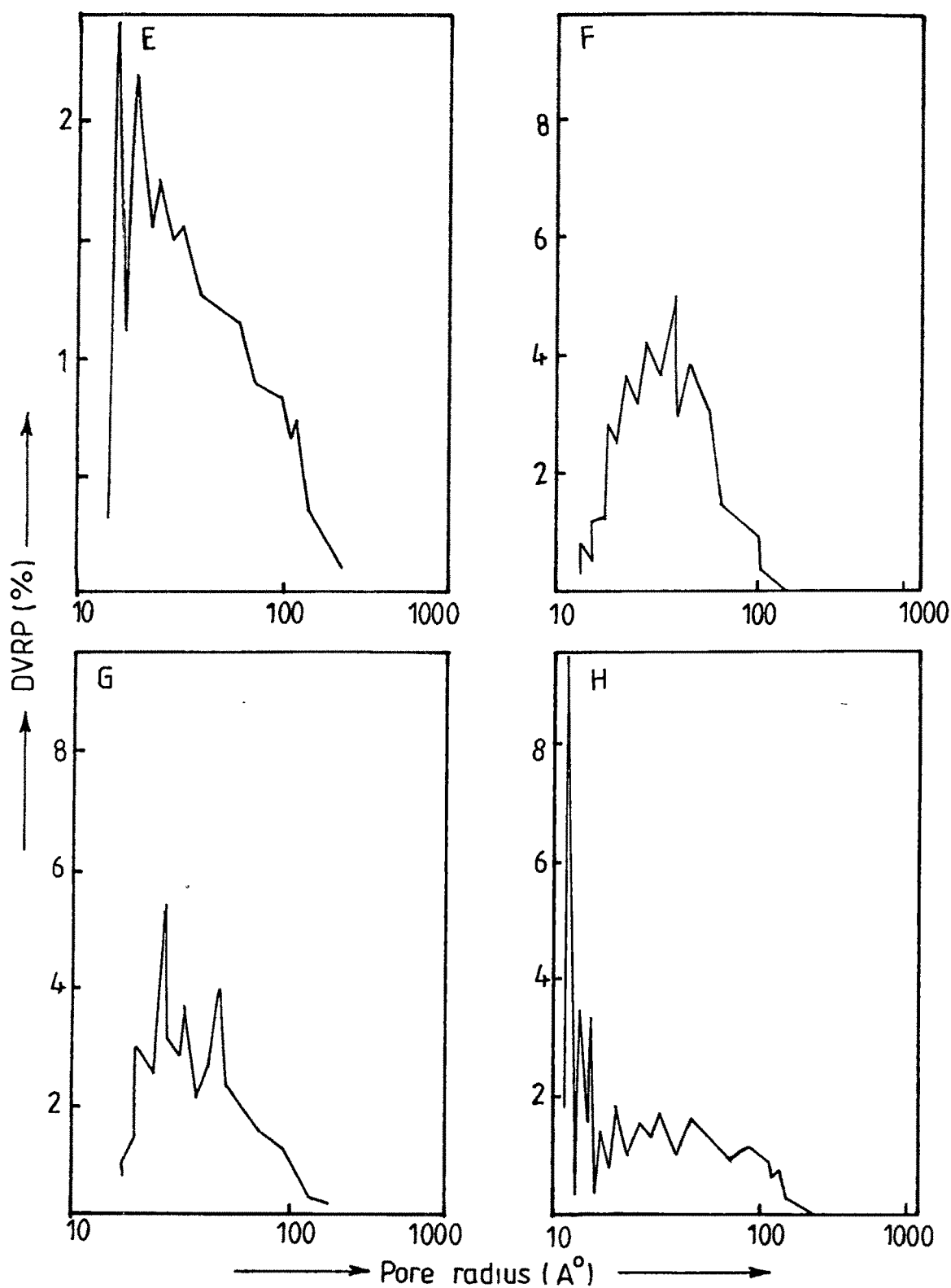


Fig III. 15. Pore size distribution curves of alumina samples.
 E. Succinic-823, F. Citric-823, G. Tartaric - 823,
 H. Adipic-823

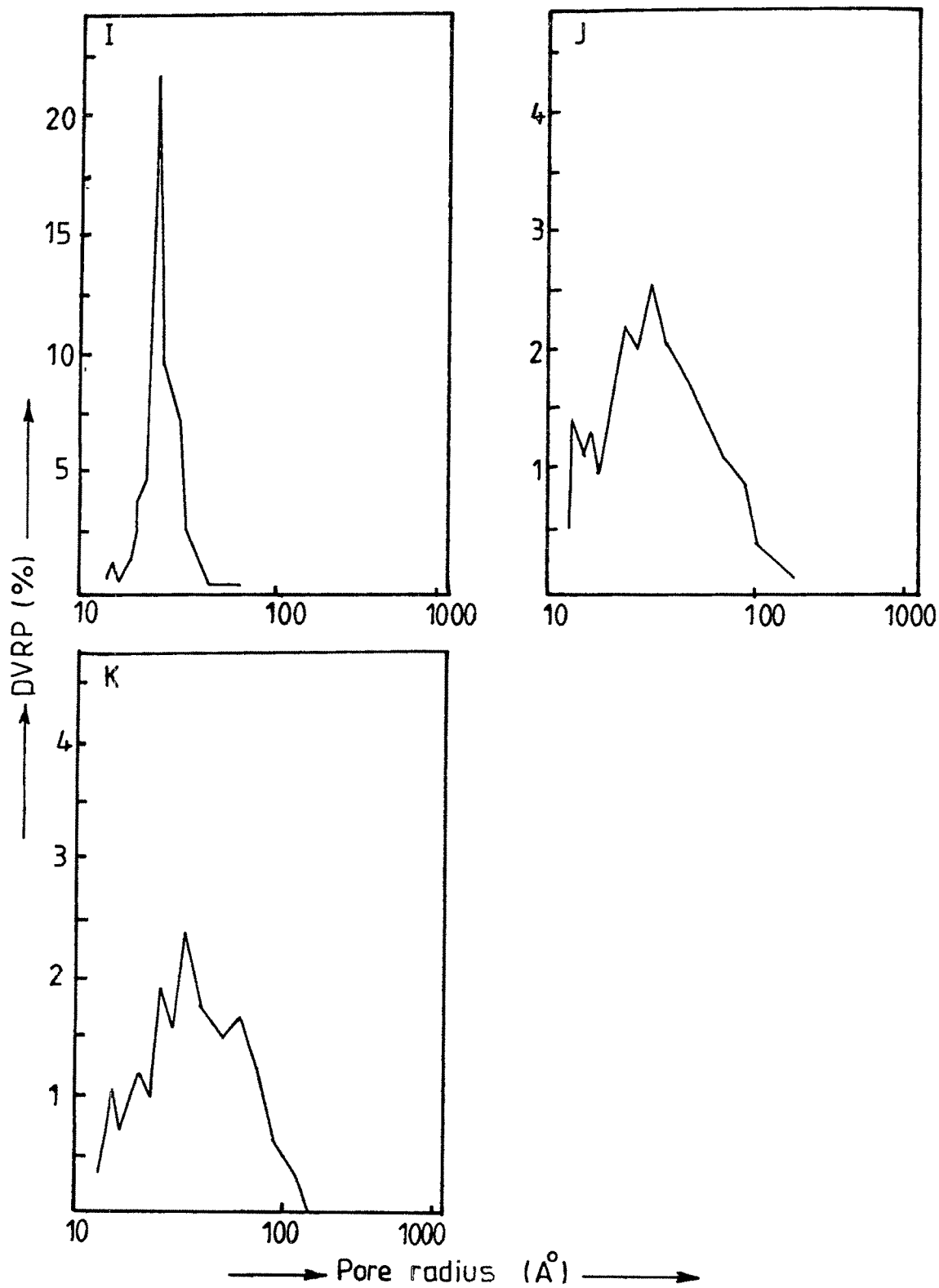


Fig. III.16 Pore size distribution curves of alumina samples.
I. CK-300, J. Propionic-823, K Maleic-823.

ammonia/g/sq. m are given in Table III.4. The TPD patterns are presented in Figures III.17,18.

The chemisorption temperature was maintained at 373 K in order to avoid physical and weak chemical adsorption. All the samples were preheated at 823 K in a flow of pure helium gas to remove the adsorbed impurities and moisture. All the samples were found to have three desorption maxima corresponding to weak, medium and strong acid sites. Eventhough the separation between the peaks are not clear, the strongest peak corresponds to weak acid sites. Strong acid sites which can retain ammonia above 773 K are absent in almost all the cases.

It is found that there exists a relation between acidity and crystallinity. The total acidity was found to decrease with increase in crystallinity. This can be anticipated considering the sintering of very small X-ray amorphous crystals into more ordered large crystals. But it is observed that the intensity of the peak corresponding to strong acid sites increases with crystallinity. A study of the alumina surfaces by Peri (122), suggests that a spinel type alumina exposes only the (1 0 0) planes on the surface. Such phases can accomodate comparatively weak acid sites only. On the other hand, phases like eta alumina contain higher proportion of strong acid sites due to the exposure of (1 1 1) plane. Similar situations can arise when aluminas are heated to higher temperatures. In such cases it is reported that from an energy point of view the (1 1 1) plane is most likely on the surface (52). The acid sites on this plane will be more stronger as in the case of eta alumina. A close

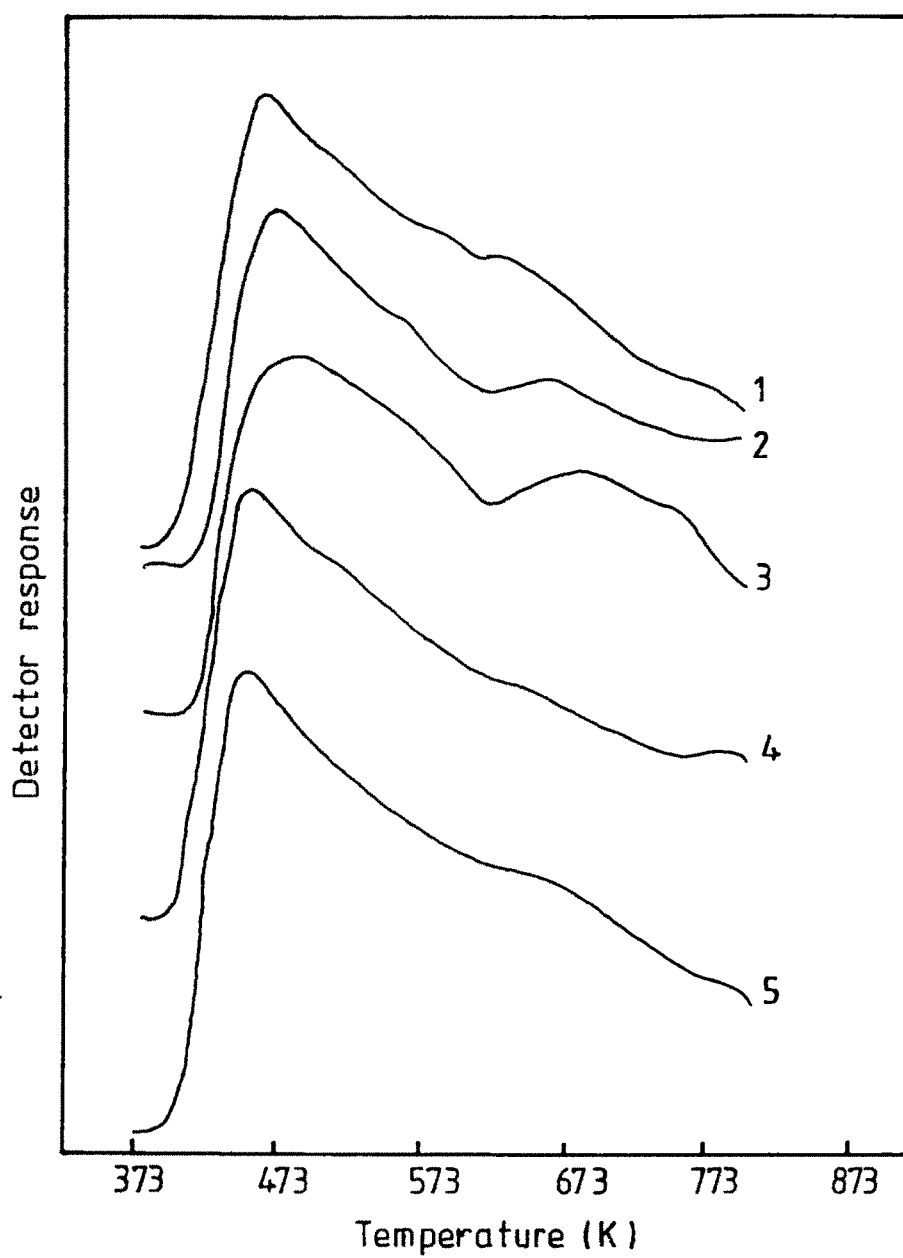


Fig.III.17. Ammonia TPD of alumina samples

1. Z-823, 2. Tartaric-823, 3. Acetic- 823
4. Malonic-823, 5. Maleic - 823.

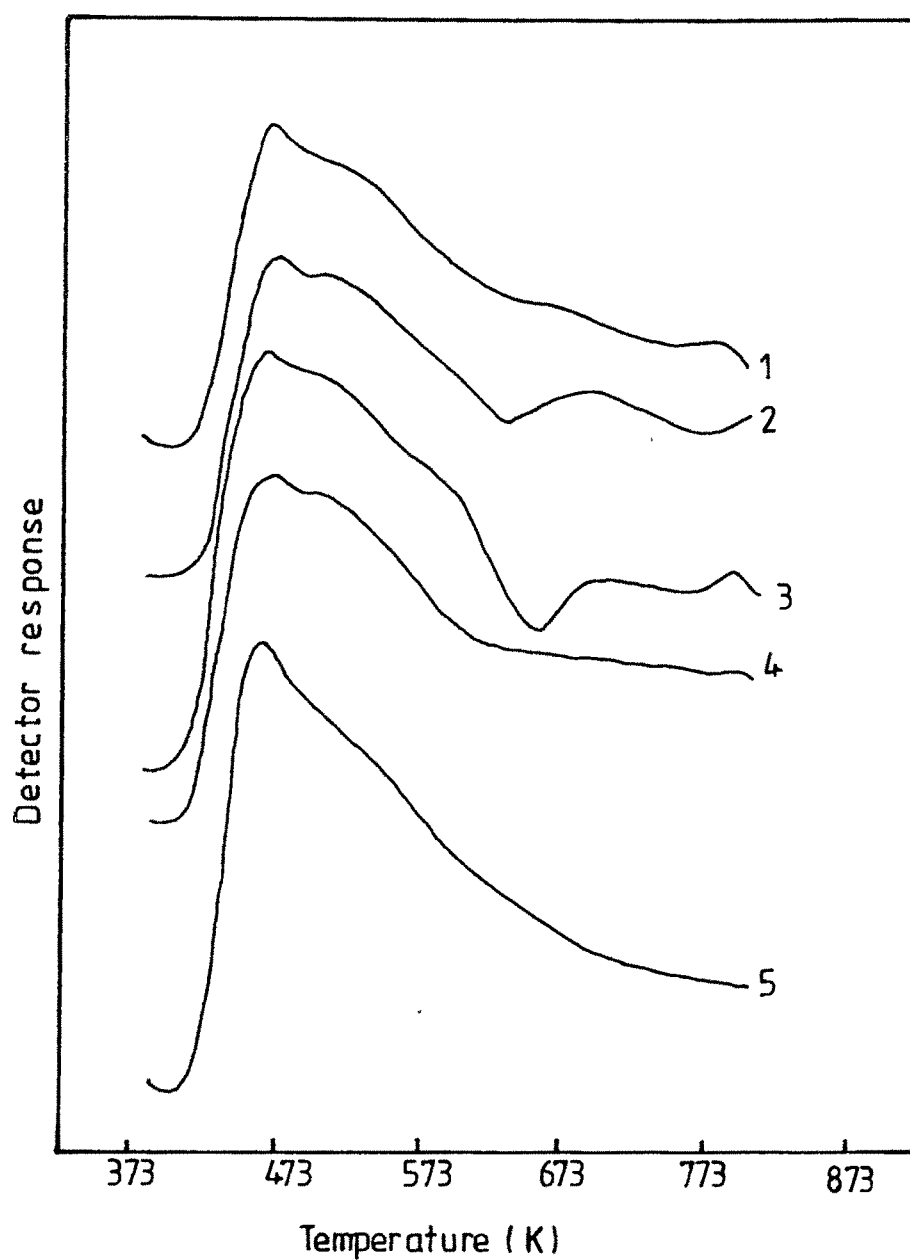


Fig.III.18. Ammonia TPD of alumina samples.
1. Citric-823 , 2. Succinic-823 , 3. Oxalic-823,
4. Adipic -823 , 5. Propionic-823.

observation of the XRD patterns in Fig.III.5,6,7 shows that the intensity of the 4.6 \AA^* band corresponding to the reflection from (1 1 1) plane is directly proportional to the intensity of the TPD peak corresponding to the strong acid sites. For example, XRD of Propionic-B23 and Malonic-B23 show very weak 4.6 \AA^* band and correspondingly the strong acid sites are almost absent in the ammonia TPD.

III.8 CONCLUSIONS

As demonstrated in the introductory discussions, various methods have been identified, which are effective in altering/modifying/controlling the textural properties of aluminas. The method of adding organic acids in comparatively small amounts during the sol preparation, is a unique one and the mode of their action is through the functional group influence. Carboxylic acids, especially di and tri basic acids are found to induce the growth of the colloidal aggregates of hydroxides in the sol, thus modifying the fundamental nature of the polymeric sol matrix. Such sols on precipitation and calcination result in alumina particles of modified size and shape. They appear to arrange themselves in a more ordered manner resulting in a decrease in the micro pore content. However, due to the generation of irregularly shaped particles/aggregates under the influence of organic acids, the meso and macro porosity increases. Thus in general, it can be concluded that this method of modification can be adopted if a reduction in micro porosity and increase in meso porosity are desired for any specific application.