Effect of heat treatment on the texture of γ-alumina

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Abstract

γ-alumina prepared from potassium aluminate was subjected to heat treatment in order to study the influence of the temperature and duration of heat treatment on the resulting texture of the catalyst.

Both specific surface area and pore volume of γ-alumina were found to depend on the conditions, employed during the heat treatment. In general, an increase in temperature or duration of heating resulted in a substantial decrease in the internal surface area and an increase in the mean pore size.

Key words : Heat treatment, texture, γ-alumina.

1. Introduction

In an earlier communication,[1] results on the effect of the method of preparation and pretreatment on the texture of alumina and related catalysts were presented. However, the texture of alumina catalysts depends to a marked extent on the crystal structure. The thermal transformations of alumina hydrates and the resulting phases depend on the temperature, rate of heating and the method employed for the preparation of the hydrate. The present investigation was undertaken to study the effect of heat treatment on the texture of γ-alumina.

2. Forms of alumina

Different terms have often been used to designate the various forms of alumina. To date three crystalline modifications of the trihydrate of alumina, $Al_2O_3.3H_2O$; and two modifications of the monohydrate, $Al_2O_3.H_2O$; are known. There is no dihydrate. Several varieties of amorphous or poorly crystalline hydrated aluminas are known. The main constituents of alumina gels are the amorphous phase and colloidal boehmite. These two phases coexist very often and the crystallized trihydrates may also appear as

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additional constituents. The crystallographic phases of the various hydrates of alumina are given below :

Crystallized hydrates of alumina

Composition	Phase	Nomenclature*
$Al_2O_3 . H_2O$	Boehmite	α-Alumina monohydrate
	Diaspore	β-Alumina monohydrate
$Al_2O_3 . 3H_2O$	Hydrargillite or Gibbsite	α-Alumina trihydrate
	Bayerite	β-Alumina trihydrate
	Nordstrandite	new β-Alumina trihydrate

* Nomenclature adopted by Aluminium Company of America.

α-hydrates are abundant in nature. The crystallized α-trihydrate in its natural state is known as gibbsite or hydrargillite. The β-trihydrate or bayerite which is not known in nature became commercially important a few years ago. It can be prepared in the laboratory by precipitation in the p_H range 10–13 from an aluminium salt or sodium aluminate. The new β-trihydrate discovered in 1956 by van Nordstrand and co-workers has not yet been isolated from alumina gel nor any specific applications were found for the same.

2.1. *Thermal transformations of alumina*

Depending on the conditions under which alumina gel is prepared from aluminium salt or alkaline aluminate, the products obtained vary widely in purity, water content, and physical characteristics. While preparing alumina gel from a salt, the resulting product primarily depends on the p_H employed during precipitation. For example, p_H less than 7 leads to the formation of impure trihydrates, while p_H equal to 8 gives pure trihydrates. At p_H equal to 9 a boehmite type gel with an average composition of Al_2O_3. $1 \cdot 5$–$2 \cdot 0$ H_2O is formed while p_H greater than 10 leads to the formation of finely crystallized trihydrates.

The thermal transformations of aluminium hydrates were comprehensively studied by x-ray powder diffraction and electron microscopy by several authors.[2-6] In general it was found that the transformation temperature is a function of the rate of heating, atmosphere of heating, hydrate particle size and purity. The various thermal transformations of alumina can be schematically represented as :

Alumina hydrate	Temperature of transformation °C				
	200	200–400	600	900–1000	1100–1200
		............χ............		........κ........	→α
α-trihydrate	air vacuum				

β-trihydrate	..............(ρ)..............η..............θ....................→α
	rehydration
	vacuum
	..............η....................θ....................→α
	air
α-monohydrate	rehydration
	..............γ....................δ....................→α
	air or vacuum

ρ— rho amorphous κ—kappa orthorhombic

χ—chi cubic θ—theta monoclinic

η—eta cubic spinel δ—delta orthorhombic

γ—gamma cubic

Of the six principal thermal transformations of alumina, three χ (chi) ; η (eta) ; and γ (gamma) are poorly crystallized and three κ (kappa), θ (theta) and δ (delta) are relatively well crystallized. There is a seventh form, ρ-alumina (rho) which may be considered as amorphous.

3. Experimental methods

3.1. *Preparation of γ-alumina*: Six moles of potassium hydroxide were dissolved in three litres of distilled water to which two moles of granular aluminium were added. After allowing time for the aluminium to dissolve, the solution was filtered to remove any insoluble matter. The filtrate was acidified with nitric acid until aluminium hydroxide just barely begins to precipitate. Precipitation was completed by bubbling a stream of carbon dioxide through the solution at room temperature. The precipitate was washed repeatedly with distilled water until the washings were neutral to litmus. The washed precipitate was dried in an air oven at 110° C. The product was identified as γ-alumina by x-ray diffraction.

3.2. *Measurement of catalyst properties*: Specific surface area of the catalyst was measured by the EGME (ethylene glycol monoethyl ether) adsorption method.[7] Pore size distribution of the catalysts was determined using an Aminco High Pressure Mercury Porosimeter and surface acidity by titration with n-butyl amine in non-aqueous media with Butter Yellow as the indicator.

4. Results and discussion

Alumina is known to develop acidity after an activation treatment. However, γ-alumina as prepared by the method given in (3.1) did not show any detectable acidity even after a prolonged heat treatment.

Specific surface area and pore volume of the catalyst heat treated at 200, 400 and 600° C for 12, 24, 36, 48, 60 and 72 hours respectively are reported in Table I. It was found that initially surface area increases substantially with the heat treatment. Thereafter it increases up to a point with an increase in the activation temperature as well as the time of activation beyond which it decreases. Between the activation temperature and time of activation, the former seems to have a more significant influence on the texture of the catalyst. The variation of surface area as a function of the time of activation at the different temperatures is presented in Fig. 1. It was found that

Table 1

Effect of heat treatment on specific surface area and pore volume of alumina

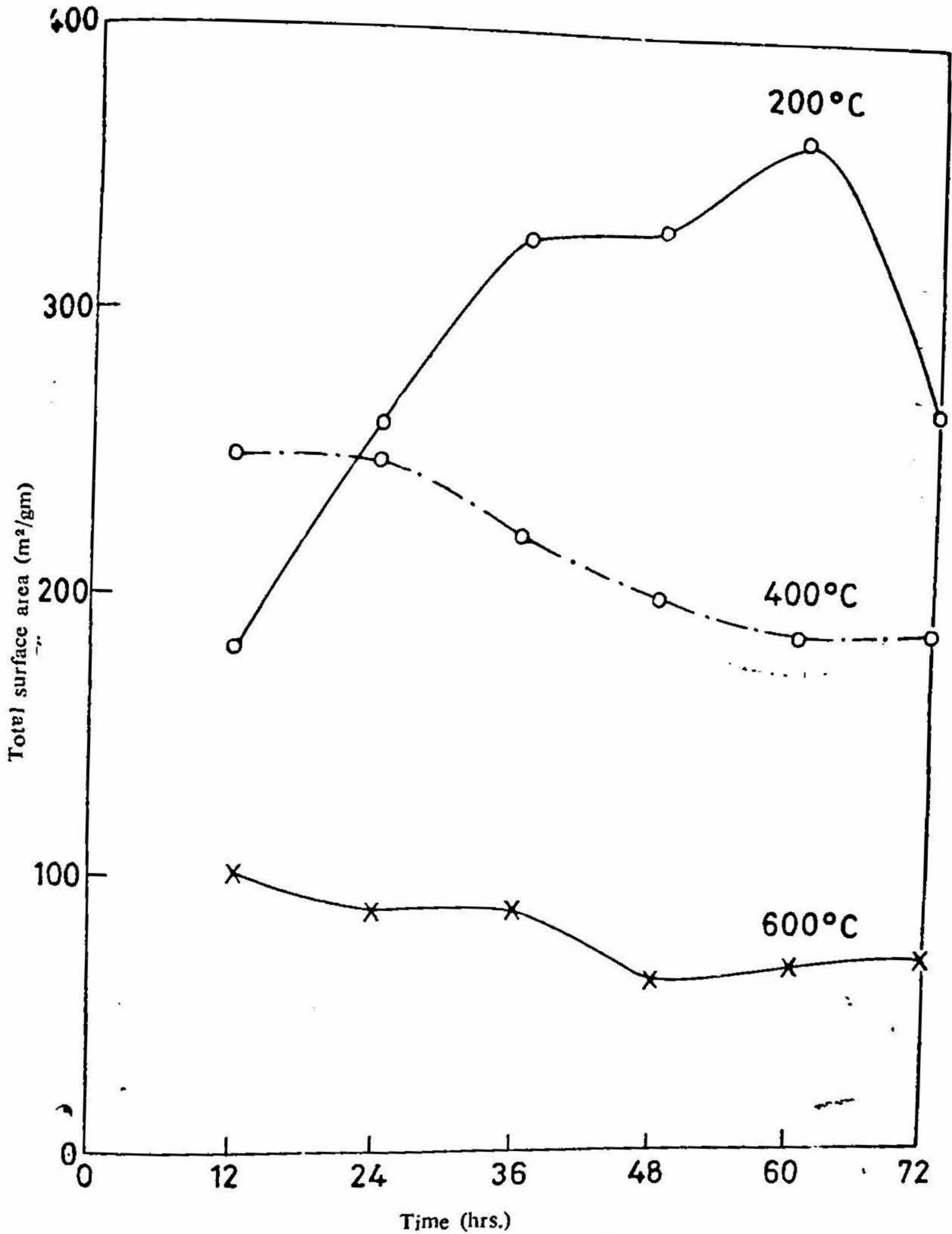| Sample	Time of heat treatment, hrs.	Surface area sq.m./g.	Pore volume c.c./g.
Commercial sample	...	82·8	0·45
Laboratory prepared sample	...	3·8	1·84
Temperature of heat treatment : 200° C			
	12	182·5	2·54
	24	261·0	2·68
	36	326·4	2·34
	48	330·8	2·48
	60	365·0	2·48
	72	268·0	2·37
Temperature of heat treatment : 400° C			
	12	249·9	2·55
	24	248·6	2·50
	36	222·5	2·53
	48	201·5	2·47
	60	187·5	2·53
	72	190·4	2·49
Temperature of heat treatment : 600° C			
	12	101·1	2·44
	24	88·6	2·38
	36	88·9	2·41
	48	63·2	2·49
	60	67·3	2·47
	72	70·8	2·49

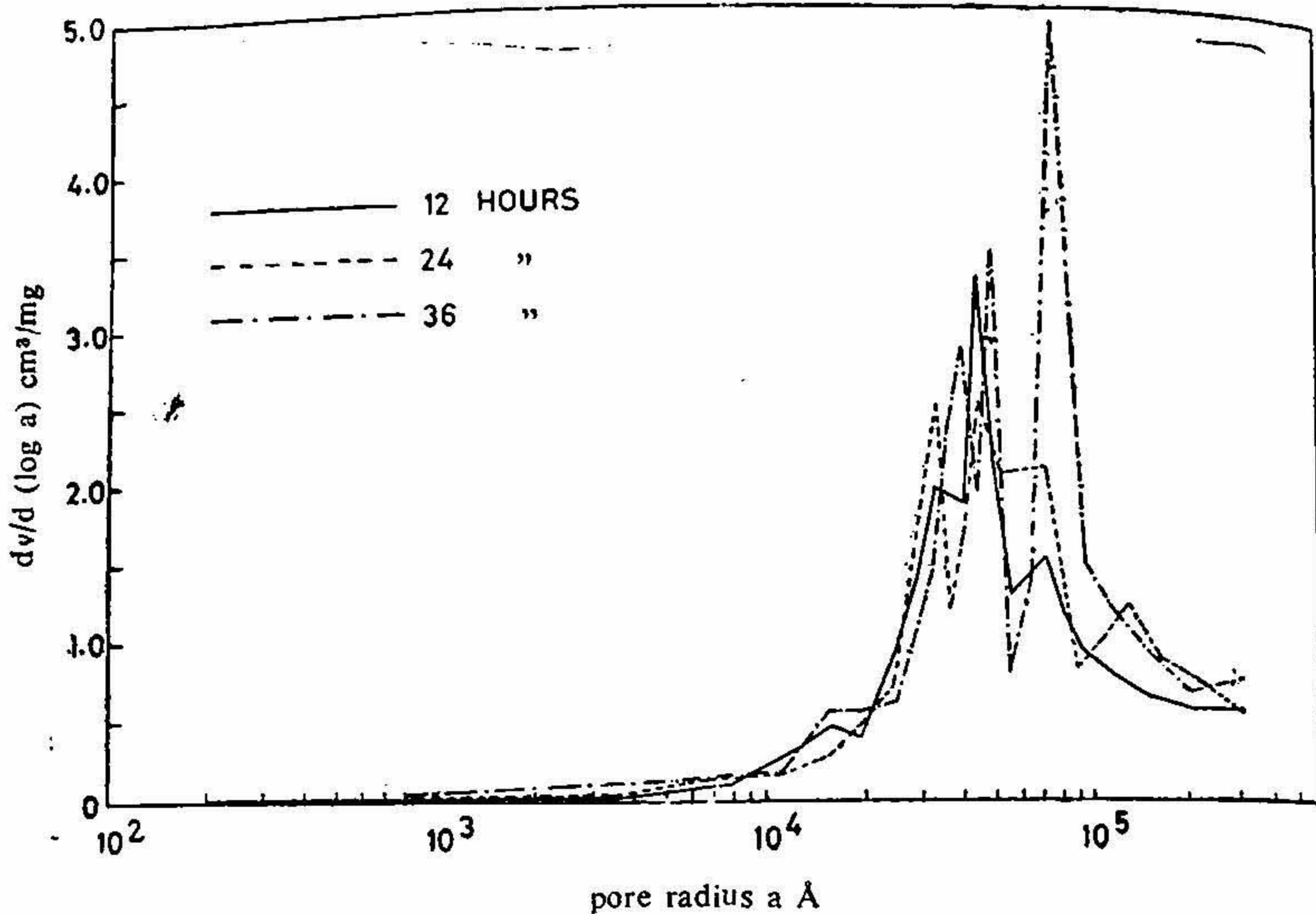FIG. 1. Effect of heat treatment on the surface area of γ-alumina.

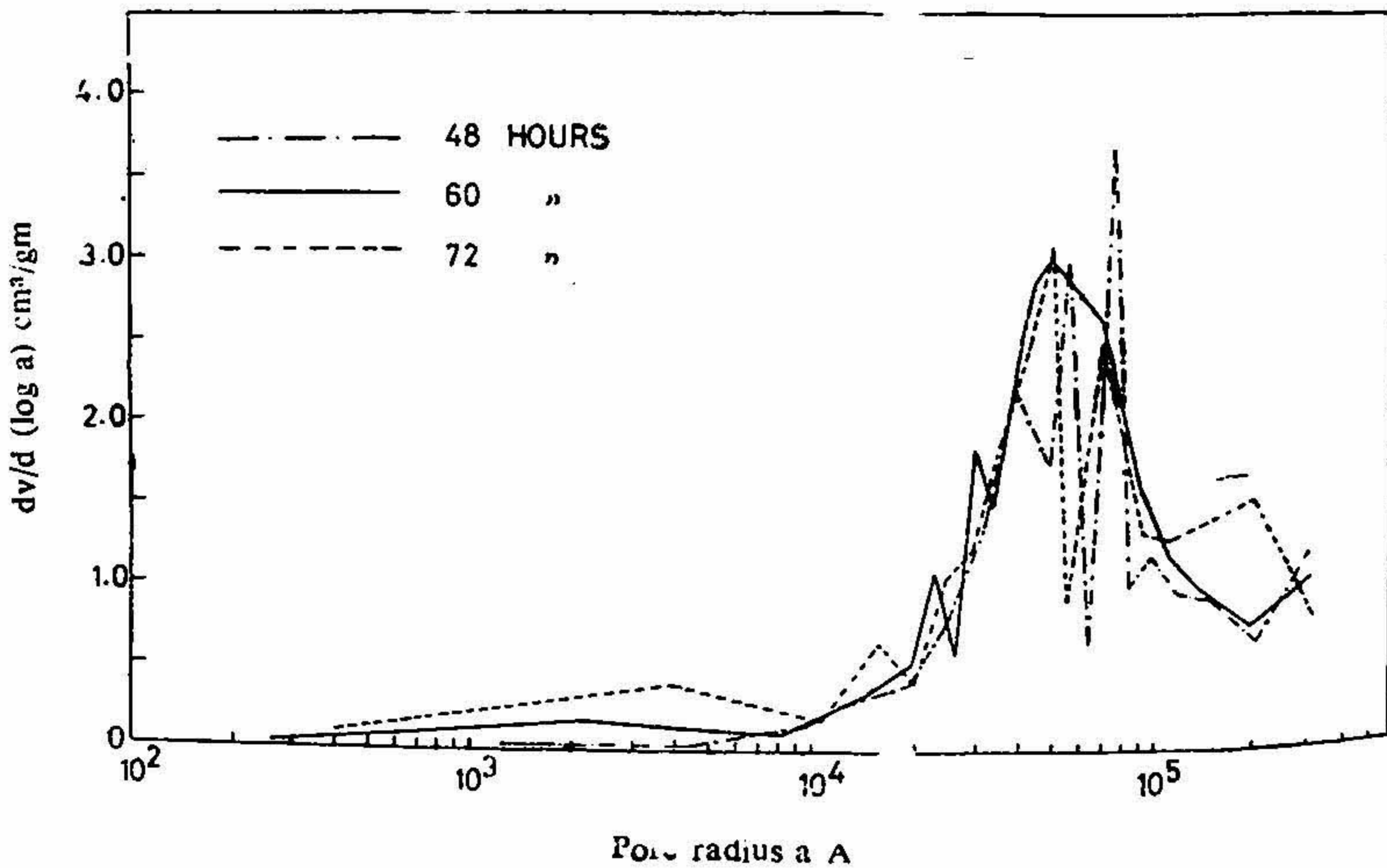FIG. 2. Pore volume distribution (γ-alumina 200° C).

FIG. 3. Pore volume distribution (γ-alumina 200° C).

maximum surface area is obtained by subjecting alumina to an activation treatment at 200° C for 60 hours. At 400° C surface area was found to decrease continuously with an increase in the time of activation, whereas at 600° C the time of activation was found to have negligible effect.

Pore volume distribution of the samples determined by the mercury intrusion method are presented in Figs. 2–8. It was found that except in the initial stages of the activation treatment, the pore volume is nearly constant irrespective of the time of activation as well as the activation temperature.

This was found to be the case with all the samples. In general, after 36 hours of activation treatment there was no significant change in the pore volume distribution. γ-alumina prepared in the laboratory was found to possess a higher surface area as well as pore volume, compared to the commercial sample.

The fall in surface area and the increase in the pore volume of γ-alumina as a consequence of the heat treatment could be either due to sintering or a loss in the bound water of alumina.[8,9] In general, most of the pore volume of the samples studied was found to lie in pores in the range $10^4 - 2 \times 10^5$ Å.

In general, an increase in the activation temperature or duration of heating resulted in a collapse of the small pores resulting in an increase in the mean pore size and a substantial fall in the internal surface area. These effects were further enhanced at activation temperatures beyond 400° C.

5. Conclusions

γ-alumina prepared from potassium aluminate did not show any detectable acidity even after a prolonged heat treatment. The poor acidity combined with the difficulty of pellatizing the same make it less attractive as an adsorbent/catalyst. It was found that γ-alumina prepared in the laboratory possesses a much higher surface area and pore volume compared to the commercial sample.

Heat treatment was found to substantially increase the surface area. However, higher temperatures and longer intervals of heat treatment resulted in a gradual decrease of surface area. Maximum surface area was obtained by heat treating γ-alumina at 200° C for 60 hours.

Heat treatment of γ-alumina, in general, resulted in a collapse of small pores giving rise to larger ones. This was more pronounced in the initial 36 hours of heat treatment. During the initial stages of heat treatment, the physical changes in the texture of γ-alumina, resulting in a greater area of adsorption for EGME is probably due to the development of cracks as the pore volume does not change and the larger pores come into existence. At higher temperatures and with more time of activation, due to increased breakdown of pores, the surface area decreases. Also, a possible sintering
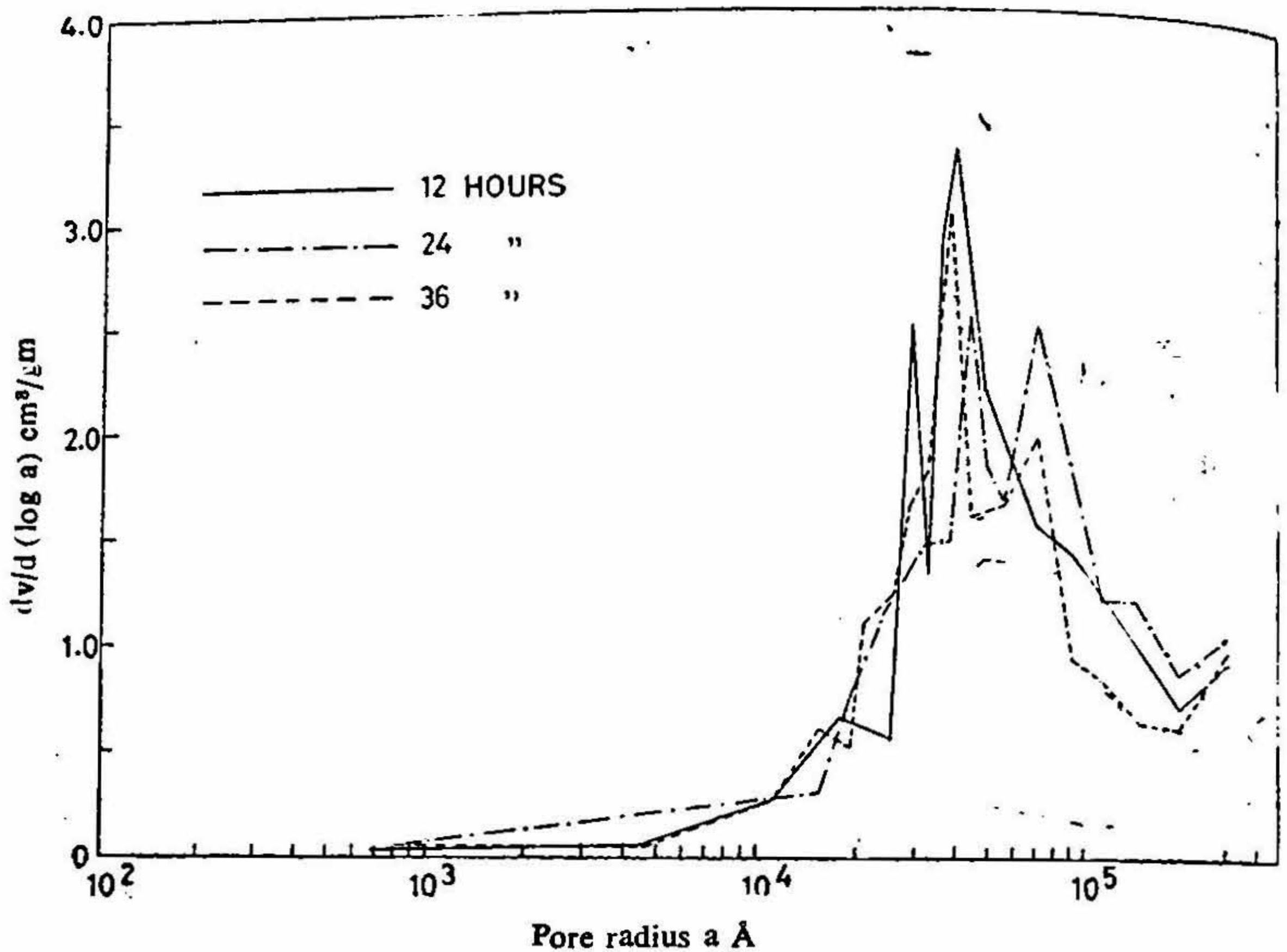
FIG. 4. Pore volume distribution (γ-alumina 400°C).

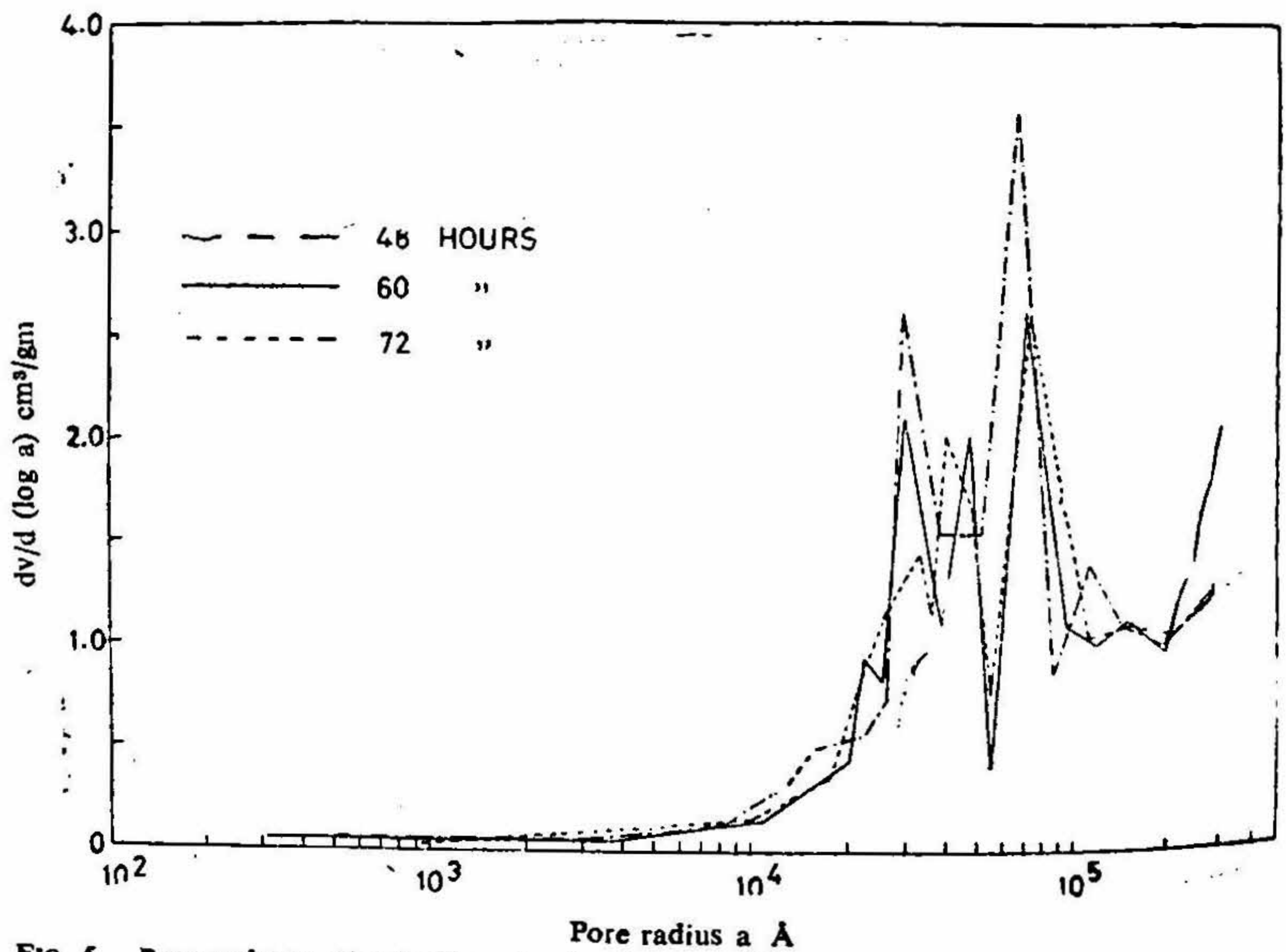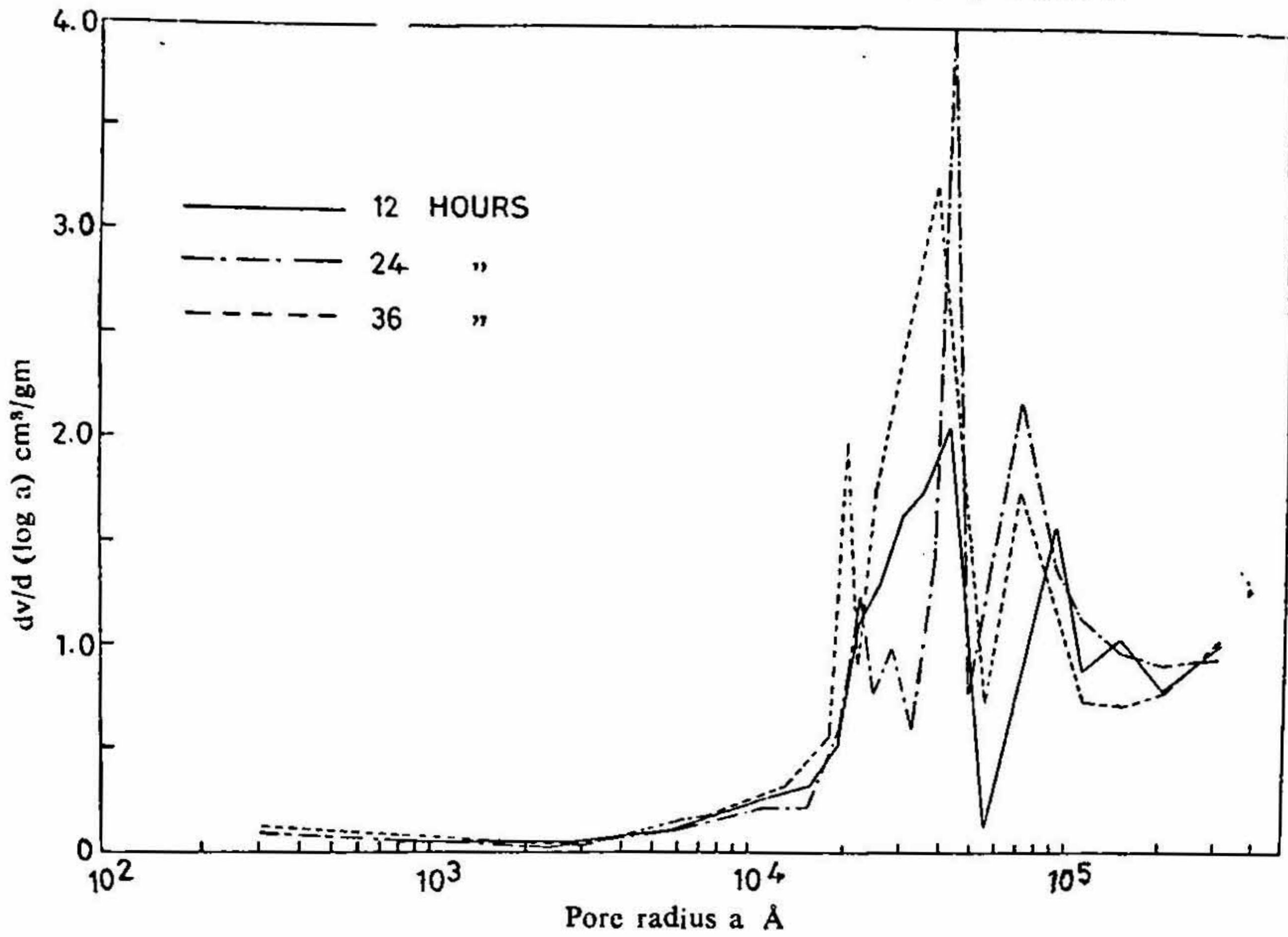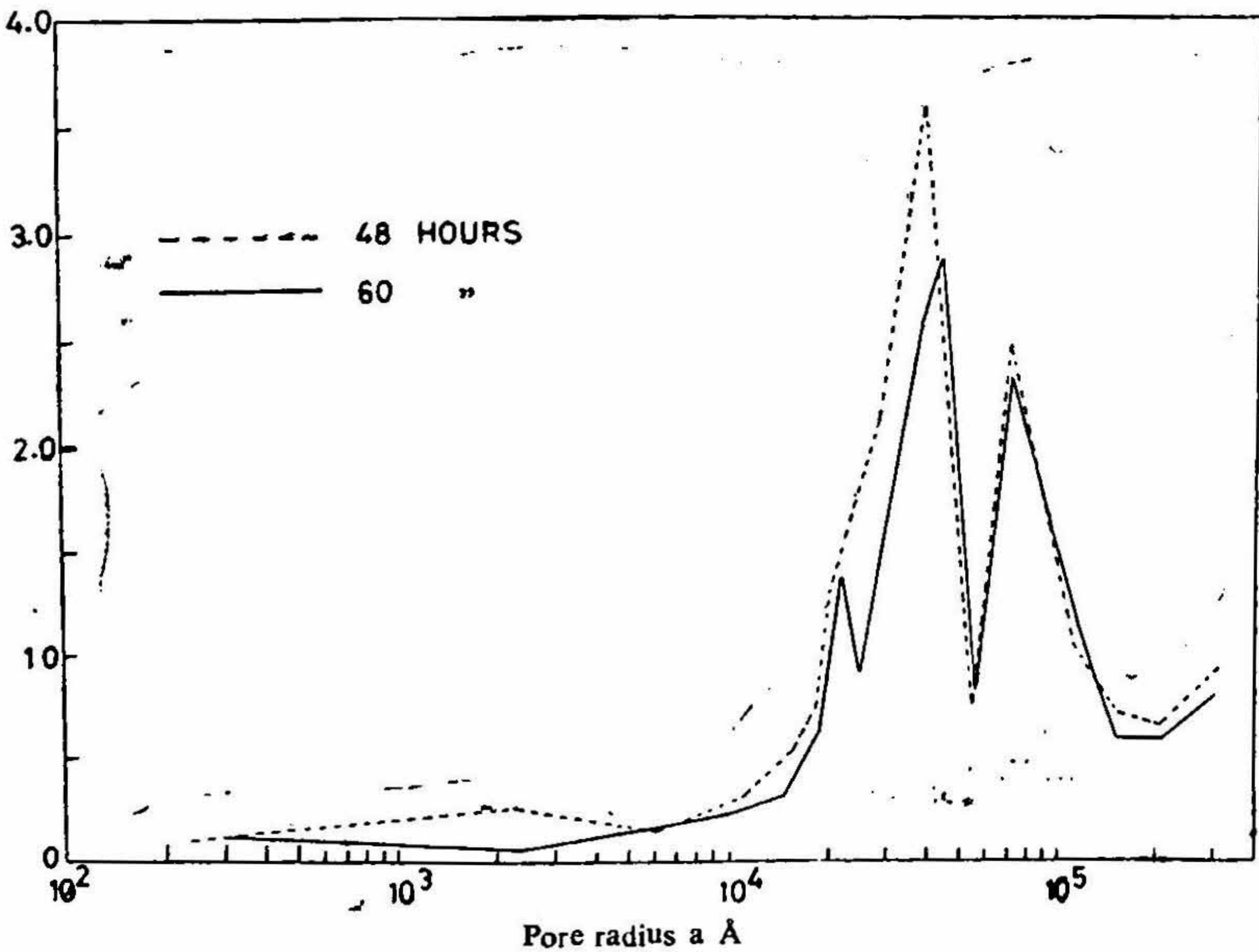FIG. 5. Pore volume distribution (γ-alumina 400°C).

FIG. 6. Pore volume distribution (γ-alumina 600° C).
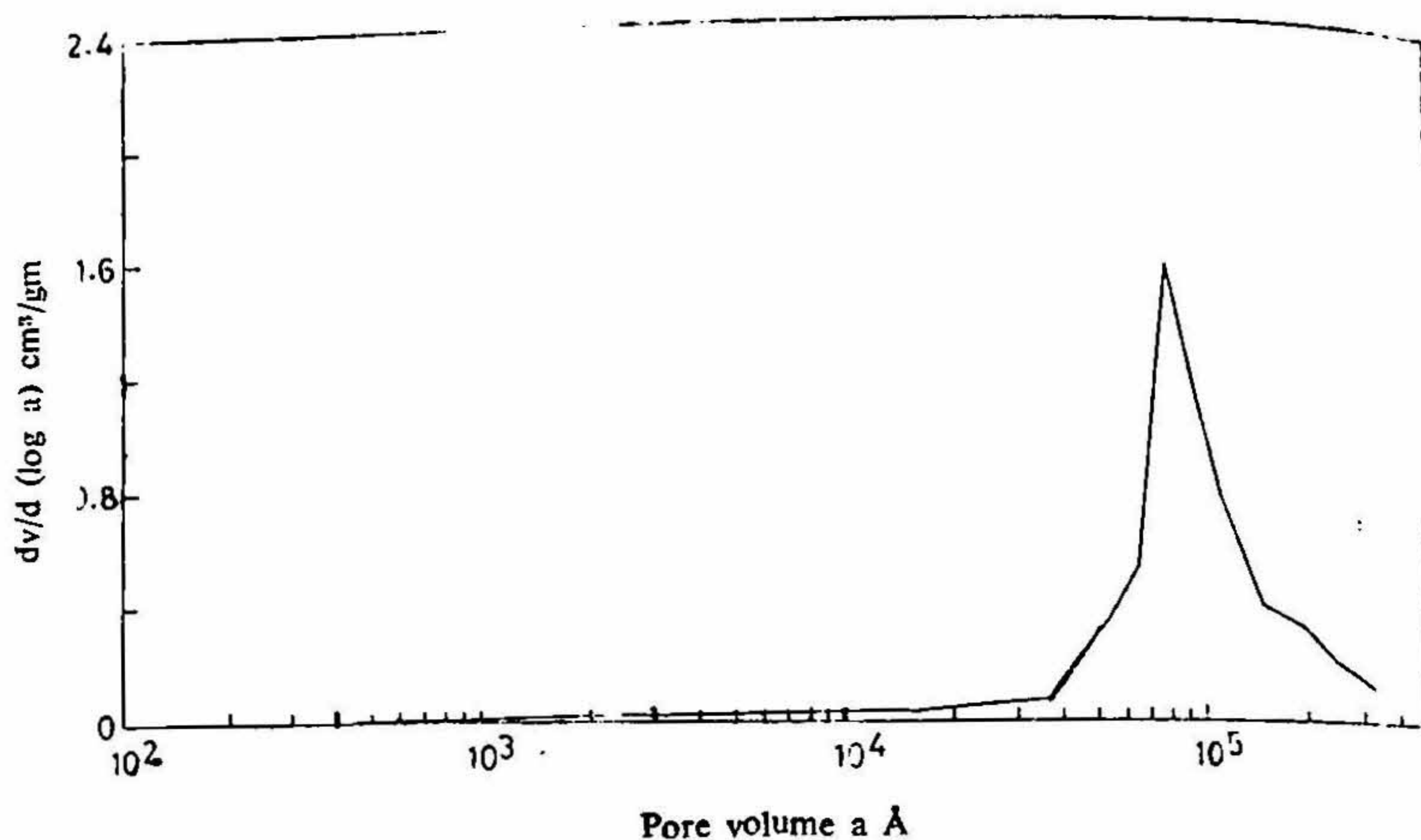

FIG. 7. Pore volume distribution (γ-alumina 600° C).

FIG. 8. Pore volume distribution (commercial γ-alumina).

action could not be ruled out as the magnitude of fractional volume at a higher pore diameter decreases with an increase in temperature and time of activation.

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